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Citation: The Journal of Chemical Physics **105**, 8142 (1996); doi: 10.1063/1.472700 View online: http://dx.doi.org/10.1063/1.472700 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/105/18?ver=pdfcov Published by the AIP Publishing

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Photodissociation dynamics of OCIO

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(Received 25 April 1996; accepted 1 August 1996)

Photofragment translational energy spectroscopy was used to study the dissociation dynamics of a range of electronically excited OClO(A^2A_2) vibrational states. For all levels studied, corresponding to OCIO($A^2A_2 \leftarrow X^2B_1$) excitation wavelengths between 350 and 475 nm, the dominant product (>96%) was ClO $(^{2}\Pi)$ +O (^{3}P) . We also observed production of Cl+O₂ with a quantum yield of up to 3.9±0.8% near 404 nm, decreasing at longer and shorter wavelengths. The branching ratios between the two channels were dependent on the OCIO(A^2A_2) excited state vibrational mode. The $Cl+O_2$ yield was enhanced slightly by exciting A 2A_2 levels having symmetric stretching+bending, but diminished by as much as a factor of 10 for neighboring peaks associated with symmetric stretching+asymmetric stretching. Mode specificity was also observed in the vibrationally state resolved translational energy distributions for the dominant $ClO(^{2}\Pi)+O(^{3}P)$ channel. The photochemical dynamics of OCIO possesses two energy regimes with distinctly different dynamics observed for excitation energies above and below $\sim 3.1 \text{ eV} (\lambda \sim 400 \text{ nm})$. At excitation energies below 3.1 eV (λ >400 nm), nearly all energetically accessible ClO vibrational energy levels were populated, and the minor $Cl+O_2$ channel was observed. Although at least 20% of the O_2 product is formed in the ground $(X^{3}\Sigma_{g})$ state, most O₂ is electronically excited $(a^{1}\Delta_{g})$. At E < 3.1 eV, both dissociation channels occur by an indirect mechanism involving two nearby excited states, ${}^{2}A_{1}$ and ${}^{2}B_{2}$. Long dissociation time scales and significant parent bending before dissociation led to nearly isotropic polarization angular distributions ($\beta \sim 0$). At excitation energies above 3.1 eV ($\lambda < 400$ nm), the Cl+O₂ yield began to decrease sharply, with this channel becoming negligible at $\lambda < 370$ nm. At these higher excitation energies, the ClO product was formed with relatively little vibrational energy and a large fraction of the excess energy was channeled into ClO+O translational energy. The photofragment anisotropy parameter (β) also increased, implying shorter dissociation time scales. The sharp change in the disposal of excess energy into the ClO products, the decrease of $Cl+O_2$ production, and more anisotropic product angular distributions at E > 3.1 eV signify the opening of a new ClO+O channel. From our experimental results and recent *ab initio* calculations, dissociation at wavelengths shorter than 380 nm to ClO+O proceeds via a direct mechanism on the optically prepared A^2A_2 surface over a large potential energy barrier. From the ClO(²Π)+O(³P) translational energy distributions, D_0 (O–ClO) was found to be less than or equal to 59.0±0.2 kcal/mol. © 1996 American Institute of Physics. [S0021-9606(96)00242-5]

I. INTRODUCTION

Experimental studies of competitive dissociation pathways following electronic excitation of small molecules provide important insight into the topography of excited state potential energy surfaces. For most simple triatomics, (NO₂, SO₂, FNO, H₂O, etc.) more than one chemical channel at commonly studied wavelengths is ruled out by thermodynamics.¹ However, there exists several small molecules which have, in addition to simple bond fission, decomposition channels involving the breaking and forming of more than one chemical bond. Formaldehyde is a benchmark system where two chemically distinct channels coexist, (i.e., H+HCO and H₂+CO), and extensive experimental and theoretical work has provided considerable insight into the dynamics of these reactions.^{2–4} Although there have been

several studies of H_2 elimination from alkenes⁵ and HCl loss from halogenated hydrocarbons,^{6,7} molecular elimination channels in heavier systems^{8,9} not involving at least one hydrogen atom is quite rare.

An interesting prospect in the excited state dynamics of molecules having multiple channels is to enhance a particular dissociation channel by selective excitation of the reactant. Bond selective photochemistry was demonstrated in CH2BrI by selecting an ultraviolet excitation wavelength corresponding primarily to a $\sigma^* \leftarrow \sigma$ transition localized on the C-Br bond.¹⁰ It was possible to preferentially break the stronger C-Br bond, leaving the weaker C-I bond relatively intact. Crim's group^{11,12} and others^{13,14} have carried out extensive studies of bond and mode specific chemistry using vibrational overtone excitation followed by electronic excitation to an excited potential energy surface. In many cases, the reactant vibrational excitation was selectively channeled into the product's vibrational degree(s) of freedom, and in favorable cases vibrationally mediated photodissociation facilitated access to regions of the excited potential energy

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surface favoring fission of a particular bond. For example, ultraviolet photodissociation of HOD $(4\nu_{OH})$ led to preferential OH bond fission, producing >15 times more OD than OH.¹²

The existence of vibrational structure in the electronic absorption spectra of fast evolving states provides another approach to studying the role of parent vibrational motion in molecular photodissociation. Reisler and co-workers¹⁵ have demonstrated that parent ClNO bending is preferentially channeled into NO product rotational excitation, and studies of CH₃ONO photodissociation has shown that reactant NO stretching vibrations are preferentially deposited into product NO vibrations.^{16,17} Recent studies of SO₂¹⁸ photodissociation have revealed the existence of mode specific SO vibrational distributions from different SO₂C(¹B₂) vibrational levels. Hepburn *et al.*¹⁹ demonstrated that the electronic state distribution of the sulfur atom product from CS₂ photodissociation depends on which band in the ¹B₂(¹\Sigma⁺_u $\leftarrow X$ ¹\Sigma⁺_g) absorption spectrum is pumped.

The studies mentioned above have demonstrated that selective excitation of well defined vibrational levels in predissociative excited states may have profound effects on product rotational, vibrational, and electronic state distributions. To date however, there have been few examples in which chemical branching ratios are strongly affected by initial nuclear motion. Earlier, mode specific Cl+O2:ClO+O branching ratios from different initial OClO(A^2A_2) vibrational levels were illustrated.²⁰ Relative to pure symmetric stretching modes ($\nu_1, 0, 0$), the Cl yield was slightly enhanced for combination bands containing one quantum of bending $(\nu_1, 1, 0)$ and significantly diminished for neighboring OClO levels having asymmetric stretching excitation (ν_1 -1,0,2). The Cl+O₂ yields from OClO photodissociation reached a peak near 400 nm, with yields of 3.9%, 3.0%, and 0.4% for the (5,1,0), (5,0,0), and (4,0,2) levels, respectively (Fig. 1). This mode specificity, leading to nearly an order of magnitude change in Cl+O₂ yields for neighboring OClO($A^{2}A_{2}$) levels, is striking in light of the fact that the levels span an energy range of only a few hundred wave numbers.²¹ Since OCIO fluorescence is negligible in this wavelength range due to picosecond dissociation time scales,²¹⁻²⁷ and since no other channels (e.g., Cl+O+O) are thermodynamically accessible,²⁸⁻³⁰ the ClO+O yields ranged from 96.1% for OCIO (5,1,0) to 99.6% for OCIO (4,0,2). Apparently, asymmetric stretching in the initially prepared parent OCIO molecule enhances simple bond fission forming ClO+O, thereby diminishing Cl+O₂ production.

The decline in Arctic and Antarctic ozone due to chemical reactions catalyzed by atmospheric chlorine has sparked considerable interest in the chemistry of halogen oxides.^{31–37} The concentration of ClO and OClO in the Antarctic stratosphere reaches levels nearly two orders of magnitude higher than normal, and these levels anticorrelate with O₃ abundance.³² It has been generally assumed³² that near ultraviolet excitation of OClO results in O–ClO bond fission (Fig. 2)



FIG. 1. OCIO absorption spectrum (204 K), from Ref. 45. Upper figure: Most intense peaks correspond to progression in symmetric stretching, ν_1 . Lower figure: OCIO(A^2A_2) vibrational assignments near 400 nm showing combination bands with one quantum of bending (ν_2) and/or two quanta of asymmetric stretching ($2\nu_3$) excitation. Vibrational assignments from Ref. 21.

$$OCIO(X^2B_1) \rightarrow OCIO(A^2A_2) \rightarrow CIO(X^2\Pi) + O(^3P).$$
(1)

Since the newly generated O atom may combine with atmospheric O_2 to reform ozone, this channel leads to a net null cycle in the atmospheric ozone budget. However, the alternative channel regenerates a reactive Cl atom

$$OClO \rightarrow Cl(^{2}P) + O_{2}(^{3}\Sigma_{g}^{-}, ^{1}\Delta_{g}, ^{1}\Sigma_{g}^{+}).$$

$$(2)$$

This channel leads to net destruction of atmospheric ozone. $^{38-41}$ According to recent estimates, if the quantum



FIG. 2. Energy level diagram for OCIO ground and excited states, and its photodissociation products.

vield for channel 2 was >0.1 across the entire OCIO absorption spectrum, it would contribute as much as several percent to the currently observed levels of ozone depletion.⁴¹ However, the relevance of OCIO photodissociation to the balance of ozone remains uncertain in the absence of complete quantum yield measurements over a range of excitation wavelengths.

The nature of the OCIO excited state potential energy surfaces and the coupling between them controls the branching between ClO+O and Cl+O₂ production.⁴²⁻⁴⁴ Spectroscopic studies^{21-26,45} have shown that the $A^2A_2 \leftarrow X^2B_1$ absorption linewidths increase steadily with v_1 (symmetric stretch) above $v_1 = 3$ in electronically excited OClO(A ${}^{2}A_{2}$) due to decreasing excited state lifetimes. Interestingly, the linewidths associated with excitation of symmetric stretching +bending $(\nu_1, 1, 0)$, or symmetric stretching+asymmetric stretching $(\nu_1, 0, 2)$, were broader at $\nu_1 = 3-7$ than those due to symmetric stretching excitation ($\nu_1, 0, 0$) alone.²¹ Although this suggests that the dissociation dynamics might be vibrationally mode specific, to date there have been no systematic studies of OCIO photochemistry as a function of A^2A_2 vibrational level.

In matrix isolation experiments at low temperature, Arkell and Schwager,⁴⁶ and others,^{47–49} reported that photolysis of OCIO led to formation of CIOO. Unlike symmetric OCIO which can be readily synthesized and studied, the ClOO peroxy isomer remains poorly characterized because of its extreme reactivity due to a very weak Cl–O₂ bond ($D_0 = 4.5$ kcal/mol).⁵⁰ Arkell and Schwager⁴⁶ suggested that the ClOO isomer resulted from recombination of the ClO+O fragment pairs in the matrix cage. Note that unlike OCIO, the ClOO isomer is transparent at $\lambda > 300$ nm and will rapidly accumulate under conditions of steady state photolysis, giving the appearance that OClO-ClOO isomerization is dominant even if ClO+O are the nascent products. Under collision free conditions in the gas phase however, recombination of the fragments is not possible and the experimental branching ratios between ClO+O and Cl+O2 must reflect the primary photochemistry.

To date, most previous studies in the gas phase^{39,40,51–56} and in solution⁵⁷ have focused on the most intense absorption peaks at $\lambda \leq 360$ nm, where $A^2 A_2$ symmetric stretching levels, $\nu_1 \ge 10$ are populated. Femtosecond time resolved studies⁵⁵ as well as CIO product state distributions⁵⁴ have been reported for a number of OCIO excitation wavelengths between 308 and 351 nm. Ruhl, Vaida, and co-workers³⁹ photodissociated gaseous OCIO using a focused dye laser near 360 nm. Absorption of additional photons from the same pulse led to multiphoton ionization of the products. Although it was concluded that $ClO(v'=4-6)+O(^{3}P)$ were the primary products, several features in the Cl⁺ action spectrum near 362 nm were taken as evidence for $Cl+O_2$ production but the quantum yield was not determined. Lawrence and Apkarian⁵¹ later studied the photodissociation of OCIO in a gas cell at wavelengths in the range 359-368 nm, and were unable to see any evidence for Cl+O₂ formation. They set an upper limit to the Cl quantum yield of $<5 \times 10^{-4}$ (0.05%) in this wavelength region.

Subsequently, Bishenden, and Donaldson (BD)^{52,53} have investigated the photodissociation of OClO near 360 nm using 2+1 REMPI at 235 nm for detection of the Cl atomic product. They concluded that Cl atoms are formed upon single photon excitation of OCIO near 360 nm, initially reporting a Cl yield of 0.15 (15%). We have studied OCIO photodissociation dynamics using photofragment translational energy spectroscopy.²⁰ In addition to the dominant ClO+O channel, we also observed Cl+O₂ from photodissociation of OCIO, but only at longer wavelengths near 400 nm. In agreement with Lawrence and Apkarian⁵¹ we were unable to see any evidence for this channel near 360 nm, but as expected did observe strong ClO+O signal. We reported an upper limit of 0.2% for the Cl+O₂ yield at $\lambda \sim$ 360 nm and concluded that the ClO+O channel accounts for >99.8% of the absorption cross section.

BD has subsequently revised their earlier value of 15% to be an upper limit, with a lower limit being a few percent.⁵³ They have also reported that the ClO+O quantum yield near 360 nm was enhanced by excitation of combination bands having two quanta of asymmetric stretching (8,0,2) or (9,0,2). Although this seems similar to our earlier observations of mode specific branching ratios at longer wavelengths, in our case the enhancement of ClO+O was accompanied by a diminished yield of Cl+O₂, and vice versa.²⁰ In the report by BD, on the other hand, the Cl REMPI spectra matched the OCIO absorption spectrum for all OCIO $(A^{2}A_{2})$ levels near 360 nm. They thus concluded that the Cl+O₂ yield was constant (i.e., at least a few percent) while the ClO+O yield was wavelength dependent.⁵³ This result is difficult to rationalize however, since fluorescence must be negligible due to picosecond dissociation time scales, and other dissociation channels are thermodynamically closed. Since product flux must be conserved, enhancement in one dissociation channel should be accompanied by a decrease in the other.

Ab initio calculations on the ground and excited electronic states of OCIO were first carried out by Gole in 1980.⁴² His calculations confirmed that the photochemical dynamics of OClO involves interactions between several different excited electronic states. From earlier spectroscopic studies, it was known that absorption between 220 and 460 nm (Fig. 1) corresponds primarily to the parallel $A^2A_2 \leftarrow X^2B_1$ transition.^{22–26} The 2B_2 and 2A_1 states lie at energies slightly below the prepared A^2A_2 state.^{42,43} Although the ${}^{2}A_{1} \leftarrow X {}^{2}B_{1}$ transition should be a dipole allowed, direct ${}^{2}B_{2} \leftarrow X {}^{2}B_{1}$ excitation is symmetry forbidden. The ${}^{2}A_{1}$, if accessed, should be strongly coupled by vibronic interactions to the "dark" strongly bent ${}^{2}B_{2}$ state which, according to Gole, could subsequently undergo concerted rearrangement in the matrix forming the peroxy Cl-O₂ isomer. Thus, direct excitation to the ${}^{2}A_{1}$ state followed by vibronic coupling to the ${}^{2}B_{2}$ was suggested as a possible mechanism for ClOO production, rather than geminate ClO+O recombination.⁴² Although subsequent spectroscopic studies^{21,45} have indicated that the ${}^{2}A_{1}$ state carries no oscillator strength in the near UV, as discussed in the next paragraph, recent theoretical work⁴³ confirms the indirect in-

Recently, Peterson and Werner carried out ab initio calculations on OClO \rightarrow ClO+O,⁴³ and in a second paper, specifically address OClO→Cl+O2.44 Cuts of their potential energy surface⁴³ are reproduced in Fig. 3. Due to the existence of a potential energy barrier for dissociation to ClO+O along the $A^{2}A_{2}$ asymmetric stretching coordinate, the low lying $A^{2}A_{2}$ levels are bound along all three normal modes and dissociation requires the involvement of other states. From the recent calculations, it was concluded that the A^2A_2 is coupled primarily to the ${}^{2}A_{1}$ by spin-orbit interactions. $OClO(^{2}A_{1})$ can subsequently dissociate through a nearly linear configuration to $ClO(^{2}\Pi) + O(^{3}P)$. Another decay mechanism for the ${}^{2}A_{1}$ state involves vibronic coupling to the strongly bent ${}^{2}B_{2}$ due to the presence of a conical ${}^{2}A_{1}/{}^{2}B_{2}$ intersection. $OClO(^{2}B_{2})$, in turn can decay by two alternative paths, to either $\text{CIO}(^{2}\Pi) + \text{O}(^{3}P)$ or $\text{Cl}(^{2}P)$ + $\text{O}_{2}(X \,^{3}\Sigma_{g}^{-}, a \,^{1}\Delta_{g}, b \,^{1}\Sigma_{g}^{+}).^{43,44}$

II. EXPERIMENT

A. The molecular beam apparatus

The experimental apparatus employs a molecular beam source which can be rotated through an angle of 90° in a vertical plane perpendicular to the (horizontal) laser axis.⁵⁸ The seeded supersonic molecular beam, described below, was collimated by two skimmers separated by a region of differential pumping, and was crossed by the unfocused output (\sim 3 mm diam) from an excimer-pumped Lambda-Physik FL2002 dye laser (0.5–10 mJ, 20 ns, 50 Hz). A fraction of the photodissociation products recoiled out of the molecular beam into an electron bombardment ionizer located 36.8 cm away from the interaction region. After ionization by 200 eV electron impact, positive ions were extracted into a quadrupole mass filter (Extrel) and counted by a Daly-type ion detector. A multichannel scaler, triggered by the laser pulse,

was used to record the product time of flight spectra at various angles between the molecular beam and detector.

B. The OCIO molecular beam

OCIO was generated by passing 5% Cl₂/He at ~760 Torr through a U tube containing NaClO2 and glass beads, as described elsewhere.^{20,59} Note that OCIO is known to be explosive under certain conditions and should be handled with great care. The mixture flowed through Teflon tubing to a piezoelectric driven pulsed molecular beam source.⁶⁰ After the NaClO₂ column was operated for some time, the $Cl_2 \rightarrow OClO$ conversion efficiency decreased and significant Cl₂ contaminant appeared in the beam. After some experimentation using various NaClO2 samples, this behavior was attributed to the drying of the column over the course of the experimental run. Apparently, the heterogeneous conversion of Cl_2 to OCIO requires the presence of some H_2O . The conversion efficiency could be increased reliably to $\sim 100\%$ by presaturating the Cl₂/He mixture with water by bubbling through room temperature water and then flowing this mixture through the NaClO₂ tube. Since the presence of water vapor was undesirable due to OClO-H2O cluster formation, the OClO/H₂O/He mixture was passed through a -10 °C trap to remove H₂O before entering the molecular beam source.

For TOF data recorded at small angles between the beam and detector axis, some time dependent background was observed in experiments using the pulsed beam when the laser was turned off. This signal results from the time dependent intensity fluctuation of OCIO background near the beam axis due to the pulsed nature of the beam. When this signal was present, parallel experiments were conducted with the laser on and off and difference spectra were employed for the analysis.



FIG. 3. Cuts of OCIO potential energy surfaces calculated by Peterson and Werner, reproduced from Ref. 43. Left figure: Dependence of potential energy on Cl–O bond length for fixed valence angle of 117.4°. Center figure: Dependence of potential energy on OCIO valence angle for fixed Cl–O bond length of 2.95 a_0 . Right figure: The effect of asymmetric bond length distortion for $r_{\text{OCI}}=2.95a_0$ and $\theta_{\text{OCIO}}=117.4^\circ$.



FIG. 4. Newton diagram in velocity space for Cl-containing fragments resulting from decomposition of OCIO A^2A_2 (5,1,0) prepared at 404 nm. Arrow denotes initial OCIO beam velocity, and circles are calculated recoil velocities for formation of ground vibrational state fragments.

C. Data analysis

The product time of flight spectra were analyzed using a version of the program CMLAB2⁶¹ running on a personal computer. The data analysis involved an iterative forward convolution method, described elsewhere.^{61(a)} Using the known apparatus functions and the measured molecular beam velocity distribution, a trial P(E) and CM angular distribution (β parameter)^{62,63} was used to calculate the TOF distribution for a fragment mass at a given molecular beam-detector angle. The calculated TOF were compared to the experimental data and then an improved P(E) was generated to better simulate the data. This procedure was continued iteratively using data obtained at several detector angles until good agreement was achieved between the experimental and simulated TOF.

The photofragment anisotropy^{62,63} (β parameter) was measured for a number of excitation wavelengths. To reduce saturation effects, TOF spectra were obtained at low pulse energies (≤ 0.5 mJ). The polarization of the laser was rotated with respect to the detector axis using a quartz double Fresnel rhomb (Optics for Research). TOF spectra were recorded and then integrated for different polarization angles in 30 degree increments.

III. RESULTS AND ANALYSIS

A. Primary channels from (5,1,0) level

Time of flight (TOF) data was recorded with the mass spectrometer set at Cl⁺, ClO⁺, O⁺, and O₂⁺. Because the detector is located away from the molecular beam axis, only the photofragments are detected in our experiments. The Newton diagram in velocity space for the Cl-containing fragments from dissociation of OCIO A ²A₂ (5,1,0) at 404 nm is shown in Fig. 4. Excitation at 404 nm (Fig. 2) prepares OCIO(A ²A₂) levels lying 11.7 kcal/mol above D_0 (O–CIO); CIO(X ²Π) may be produced in vibrational levels up to v''=4. We observe Cl⁺ signal (m/e=35) from two different sources. The dominant source is from fragmentation of CIO (from CIO+O channel) in the electron bombardment ionizer, and the minor source is from the Cl+O₂ channel. Since the



FIG. 5. Upper: CIO product TOF spectrum (20°) recorded at m/e = 51 for OCIO A ${}^{2}A_{2}$ (5,1,0) level. Middle: CI product TOF spectrum recorded under identical conditions. Dominant slower peak results from fragmentation of CIO to Cl in ionizer. Inset shows expanded vertical scale (×15) and Cl+O₂ yield. Bottom: O₂ TOF spectrum recorded under identical experimental conditions. In all figures, solid line is optimized fit to experimental data.

reaction OCIO \rightarrow CI(${}^{2}P_{3/2}$)+O₂($X \, {}^{3}\Sigma_{g}^{-}$) is nearly thermoneutral (Fig. 2), and because a large potential energy barrier exists along the reaction coordinate, a relatively large translational energy release is anticipated. For each excitation wavelength, TOF data was obtained for each product species at several different angles and the entire data set was used in the analysis. By observing both momentum matched counterfragments (i.e., CIO+O or Cl+O₂) and by determining the TOF at several different angles, we can monitor both product channels with comparable sensitivity and can directly measure the Cl+O₂:CIO+O branching ratios.

The TOF data obtained with the mass spectrometer tuned to m/e=51 (ClO⁺) and m/e=35 (Cl⁺) at 20° is shown in the upper panels of Fig. 5. The solid lines are the calculated TOF based on the optimized product translational energy distribution P(E), described below. The large slow component at 200–600 μ s is identical to that seen for ClO⁺ and results from fragmentation of CIO to Cl⁺ in the ionizer. The small, fast contribution seen at $\sim 120 \ \mu s$ in the Cl data is from the Cl+O₂ channel. In the inset to the Cl TOF at 20° (Fig. 5), the vertical scale for the $Cl+O_2$ peak is expanded by a factor of 15 at $T = 140 - 200 \ \mu s$. The bottom panel of Fig. 5 shows the O_2^+ TOF resulting from the Cl+O₂ channel. Figure 6 shows the O^+ TOF recorded at 40° and 70°. This signal results exclusively from O atoms from the ClO+O channel since the ClO is constrained to $\theta < 40^{\circ}$. Contribution from fragmentation of O_2 (from the Cl+O₂ channel) to O⁺ in the detector is negligible.

The entire data set for each wavelength was fitted to a single P(E) for each channel. The P(E) for the ClO+O channel was primarily derived from the O⁺ data since the TOF for the faster light fragment showed the most resolvable structure. The solid lines in the TOF spectra were calculated



FIG. 6. O atom TOF spectra recorded at indicated angles for CIO+O channel from (5,1,0) level. Structure corresponds to vibrational excitation of CIO counterfragment.

using the translational energy distributions [P(E)'s] shown in Fig. 7. The maximum calculated translational energies for formation of vibrationally excited diatomic molecules are indicated. The structure in the P(E) for the ClO+O(³P) channel clearly corresponds to a progression in ClO X ² Π (v''). From conservation of energy:

$$E_{\text{photon}} + E_{\text{int,OCIO}} = D_0(\text{O-CIO}) + E_{\text{trans,CIO+O}} + E_{\text{int,CIO}} + E_{\text{int,OI}}$$
(3)

Pulsed expansion of 10% OCIO in He at 1 atm should result in substantial rotational cooling. Since the laser was tuned to assigned the OClO $A^{2}A_{2}(v_{1},v_{2},v_{3})$ peaks to $\leftarrow X^2 B_1(0,0,0)$ transition, hot-band contributions are negligible so $E_{int,OCIO} \sim 0$. For all spectra reported here, the laser was tuned to OClO peaks corresponding to absorption of the ³⁵Cl isotope.²¹ At λ >274 nm only O(³P_I) is thermodynamically accessible: The ground spin-orbit state of oxygen atom is ${}^{3}P_{2}$ and excited levels lie at 158 cm⁻¹ (${}^{3}P_{1}$) and 227 $\text{cm}^{-1}({}^{3}P_{0})$.²⁸ The O(${}^{3}P$) fine structure splitting is smaller than the spacing between ClO product vibrational energy levels (850 cm⁻¹) and the two ClO(X ${}^{2}\Pi_{1/2,3/2}$) spin-orbit levels (350 cm^{-1}) ²⁹ Thus we are only able to resolve ClO vibrational structure but some finer detail can be partially resolved at low translational energies where our resolution is greatest (e.g., Fig. 7). Since we resolve ClO vibrational structure, the data can be used to check for possible dependence of the ClO fragmentation pattern on its vibrational level. From momentum conservation, the O atom carries the same P(E) information as the ClO fragment. If highly vibrationally excited ClO levels were, for example, more exten-



FIG. 7. Translational energy distributions for $O({}^{3}P)+CIO$ and $CI({}^{2}P)+O_{2}$ channels from $A {}^{2}A_{2}$ (5,1,0) level. The calculated maximum relative translational energies for production of internally excited diatomics are indicated.

sively fragmented in the ionizer, the observed intensities of the slowest CIO products would be smaller than predicted from a P(E) derived independently from the O atom TOF. Since good agreement was found between the P(E) derived from the O and CIO TOF data, we conclude that the CIO fragmentation pattern is not very sensitive to vibrational level for v = 1-5, apparently because this level of CIO internal excitation is relatively small and CIO⁺ is a rather strongly bound ion.

The P(E) for the Cl+O₂ channel (Fig. 7, lower) is structured, showing two distinct components. Since the only accessible excited Cl atomic state²⁸ is ${}^{2}P_{1/2}$ at 881 cm⁻¹, the structure and width of the P(E) primarily reflects the O₂ internal state distribution. In Fig. 7, the maximum translational energy for formation of various vibrational levels of $O_2(X \, {}^{3}\Sigma_{g}^{-})$, $O_2(a \, {}^{1}\Delta_{g})$, and $O_2(b \, {}^{1}\Sigma_{g}^{+})$ are indicated. By energy conservation, the contribution at 41 < E < 67 kcal/mol must correspond to production of Cl+O₂(X ${}^{3}\Sigma_{g}^{-})$. As discussed later, the sharp rise below 41 kcal/mol is attributed to dominant production of $O_2(a \, {}^{1}\Delta_{g})$.

Figure 8 shows the Cl⁺ TOF spectrum showing the relative contribution for both channels while varying the photolysis laser pulse energy. The signal intensity is proportional to the pulse energy from 0.5-10 mJ/pulse, as expected for a one photon process. More importantly, the *shape* of the TOF and the relative contribution from the two channels were constant over this range of laser energies, demonstrating that multiphoton effects are negligible under our experimental

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FIG. 8. Power dependence for Cl TOF spectra recorded at 20° for photodissociation of OCIO A ${}^{2}A_{2}$ (5,1,0).

conditions using an unfocused nanosecond dye laser.

B. CIO:CI detection sensitivity

The relative detection sensitivity for CIO and Cl was determined directly by photodissociation⁶⁴ of CIOCl,

$$ClOCl \rightarrow Cl(^{2}P) + OCl(^{2}\Pi).$$
(4)



FIG. 9. CIO and CI TOF spectra for CIOCI photodissociation at 423 nm.



FIG. 10. Photodissociation of ClOCI. Top: Dependence of ClO signal intensity with laser polarization angle. Bottom: ClO+Cl product translational energy distribution for photodissociation of ClOC1 at 423 nm.

The TOF data for CIO^+ and CI^+ resulting from 423 nm photodissociation of CIOCI at 20° and 50° is shown in Fig. 9. As expected, one peak was seen in the CIO TOF, whereas two peaks appeared for m/e = 35 (Cl⁺). The slower peak at Cl⁺ results from fragmentation of CIO in the ionizer, and the fast peak in the Cl⁺ TOF results from the Cl atom recoiling from ClO. The P(E) for the ClO+Cl channel, obtained by fitting all three TOF spectra, is shown in Fig. 10. The anisotropy parameter (β) was found to be ~ -1.0 by measuring the Cl signal intensity as a function of laser polarization angle (Fig. 10, upper). This result is consistent with recent calculations⁶⁵ indicating that the absorption in this wavelength region corresponds to a perpendicular $B_1 \leftarrow A_1$ transition.

According to Eq. (4) equal numbers of Cl and ClO products must be formed from ClOCl photolysis. After fitting the two peaks to a single P(E) and after properly accounting for the differing transformation Jacobians between the lab and CM reference frames for the two fragments, we obtain the relative detection sensitivity $S_{expt}=0.32$ for the ClO and Cl fragments from ClOCl dissociation. Using this quantity, the measured ClO fragmentation pattern, and the relative contributions for the two channels in the Cl TOF from OClO photodissociation, we may calculate the Cl:ClO branching ratios for OClO photodissociation.

The relative detection sensitivity 8,66 $S_{\rm expt}$ is given by

$$S_{\text{expt}} = \frac{\sigma_{\text{ion}}(\text{ClO})}{\sigma_{\text{ion}}(\text{Cl})} \times \frac{F(\text{Cl}^+/\text{ClO})}{F(\text{Cl}^+/\text{Cl})} = 0.32.$$
(5)

In Eq. (5), $\sigma_{ion}(CIO)$ and $\sigma_{ion}(CI)$ are the 200 eV electron impact ionization cross sections for CIO and Cl, respectively. The fraction of ionized ClO fragments to yield Cl⁺ is $F(Cl^+/CIO)$ and the fraction of ionized Cl fragments yielding Cl⁺ is $F(Cl^+/Cl)=1$. Since all of the parameters in Eq. (5) may be determined directly (see below), we may also calculate $S(S_{calc})$ using values for σ and F, and compare it to our experimental value (S_{expt}). By monitoring the ClO fragment from OCIO photodissociation at Cl⁺, ClO⁺, and O⁺, we found that $F(Cl^+/ClO)=0.24$. The following empirical relationship^{8,66,67} relates the peak ionization cross section, $\sigma_{ion}(Å^2)$ to molecular polarizability, α (Å³):

$$\sigma_{\rm ion} = 36\sqrt{\alpha} - 18. \tag{6}$$

Using the known⁶⁸ atomic polarizabilities and approximating the ClO polarizability as the sum of its constituent atomic polarizabilities, we calculate $\sigma_{\text{ClO}}=43.3$ Å² and $\sigma_{\text{Cl}}=34.0$ Å². Inserting these quantities into Eq. (6), we find that $S_{\text{calc}}=0.30$, which is within 20% of the experimental value. We have used the experimental value (S_{expt}) in all calculations below.

C. Determination of CI:CIO branching ratio

The CI:CIO branching ratio from OCIO photolysis was determined from the m/e=35 (Cl⁺) TOF spectra. The relative contributions from the two channels in the Cl⁺ TOF data at 20° (Fig. 5, middle) provides the apparent branching ratio $(R_{\rm app})$, uncorrected for the detection sensitivities at m/e=35. For OCIO (5,1,0), $R_{\rm app}=0.125$. The actual branching ratio R is obtained from $R_{\rm app}$ by multiplication by the detection sensitivity S(=0.32):

$$R = \frac{\phi(\text{Cl}+\text{O}_2)}{\phi(\text{Cl}\text{O}+\text{O})} = R_{\text{app}} \times S.$$
(7)

In Eq. (7), $\phi(\text{Cl}+\text{O}_2)$ and $\phi(\text{ClO}+\text{O})$ are the photochemical quantum yields. After inserting R_{app} and *S*, we find that R = 0.040 for OCIO (5,1,0). Since OCIO fluorescence is negligible at these wavelengths due to picosecond dissociation timescales,^{24,25} $\phi(\text{Cl}+\text{O}_2) + \phi(\text{ClO}+\text{O}) = 0.99 - 1.0$, so we conclude $\phi(\text{Cl}+\text{O}_2) = 0.039$ and $\phi(\text{ClO}+\text{O}) = 0.961$. The relative $\text{Cl}+\text{O}_2$ quantum yields for different OCIO vibrational levels should be accurate to within $\pm 10\%$. From the good agreement between the experimental and calculated value of *S*, the uncertainty in the relative detection efficiency for Cl and ClO is also $\pm 10\%$. Thus the total uncertainty in our Cl+O₂ quantum yield should not exceed $\pm 20\%$ of the stated value.

D. Mode specificity at λ >400 nm

The O⁺ TOF (40°) for the cluster of OCIO($A^2A_2 \leftarrow X^2B_1$) absorption peaks near 410 nm are shown in Fig. 11. Except for the laser wavelength, the data for each TOF spectrum was obtained under identical experimental conditions. The significantly different shapes for each TOF reflect

FIG. 11. TOF spectra (40°) recorded at m/e = 16 (O⁺) for OCIO A ²A₂ (5,0,0), (4,0,2), (5,1,0), and (4,1,2). Solid line is calculated fit to the data using P(E) shown in Fig. 13.

the strong dependence of ClO vibrational distribution on the initial OClO(A^2A_2) vibrational level. In Fig. 12, the Cl⁺ TOF spectra recorded at 20° are shown for the same group of OCIO absorption peaks—in the insets the vertical scale is expanded by a factor of 15 to reveal structure in the TOF for the $Cl+O_2$ channel. The $Cl+O_2$ yields are tabulated in Table II. The data was fitted using the same procedure outlined above, using data shown in Figs. 11 and 12, as well as that obtained at other angles. The optimized translational energy distributions for the ClO+O channel are shown in Fig. 13. As shown in Fig. 12, although the Cl yield under the (5,1,0)peak is slightly greater than that seen under the (5,0,0), this channel is nearly absent under the (4,0,2). Thus, near 400 nm, the $Cl+O_2$ yield is strongly diminished by parent OCIO asymmetric stretching excitation. Note however that the shapes of the Cl+O2 TOFs are nearly independent of the OCIO vibrational mode, indicating that the O₂ internal state distributions are not significantly dependent on OClO A ${}^{2}A_{2}$ vibrational level. Indeed, the P(E) obtained for the Cl+O₂ channel from the (5,1,0) level (Fig. 7, lower) also provided a satisfactory fit for the (5,0,0) and (4,0,2) TOF spectra.

From the translational energy distributions such as those shown in Fig. 13, we have estimated the ClO vibrational energy distributions from each OClO(A^2A_2) state. In cases where the vibrational structure is fairly well resolved [e.g., (5,1,0)], vibrational distributions were determined from the relative areas under each vibrational component. In other cases, the ClO+O P(E) distributions were each fit to a sum of Gaussians. The widths of the vibrational contours in the





FIG. 12. TOF spectra (20°) recorded at m/e=35 (Cl⁺) for OCIO A ²A₂ (5,0,0), (4,0,2), (5,1,0), and (4,1,2). Solid line is calculated fit. Note that the Cl+O₂ channel is strongly suppressed for A ²A₂ levels having asymmetric stretching excitation.

P(E) are a convolution of the ClO rotational, ClO spinorbit, and O spin-orbit distributions. Since these individual contributions are unknown, ClO rotational distributions cannot be extracted from our data. The approximate ClO vibrational energy distributions are summarized in Tables I and II, together with $\langle f_v \rangle$, the fraction of available energy deposited into ClO vibration

$$\langle f_v \rangle = \frac{\Sigma_v N_v E_v}{E_{\text{avl}}}.$$
(8)

In Eq. (8), N_v is the relative yield of each vibrational level v of energy E_v above zero (for v=0), and E_{avl} is the total available energy where $E_{avl}=E_{h\nu}-D_0$ (O–ClO).

The O⁺ TOF for the cluster of OCIO peaks near 420 nm is shown in Fig. 14. Again, the CIO internal state distributions are strongly dependent on the initial OCIO vibrational mode (Fig. 15). As shown in Fig. 16, the yield of $Cl+O_2$ products decreases somewhat, and can only barely be seen in the unexpanded TOF spectra. Interestingly, the $Cl+O_2$ channel is not diminished to as large an extent under the (3,0,2) relative to its neighbors as it was for the (4,0,2). Also, the yield under the (3,1,2) is significant, in contrast to the (4,1,2) where very little $Cl+O_2$ was observed. Furthermore, the $Cl+O_2$ yield for the (4,0,0) level seems anomalously small relative to that for the (3,0,0) and (5,0,0) levels. The shape of the $Cl+O_2$ component for the (3,1,2) band is similar to that seen for the (5,0,0) and (5,1,0), with the intensity of the



FIG. 13. Translational energy distributions for $O({}^{3}P)$ +CIO channel from A ${}^{2}A_{2}$ (5,0,0), (4,0,2), (5,1,0), and (4,1,2) levels. The calculated maximum relative translational energies for production of internally excited CIO is indicated.

fastest component near 110 μ s (O₂, $X^{3}\Sigma_{g}^{-}$) approximately half that of the slower component (O₂, $a^{1}\Delta_{g}$). However, for the (4,0,0) and (4,1,0) bands, the intensities of both of these peaks are nearly identical showing that the yield of ground state O₂($X^{3}\Sigma_{g}^{-}$) relative to excited ($a^{1}\Delta_{g}$) has increased for these OCIO($A^{2}A_{2}$) vibrational levels.

At longer wavelengths, we observed a steadily decreasing contribution from the Cl+O2 channel. As summarized in Tables I and II, a relatively large fraction of available energy continues to be channeled into ClO vibrational excitation at these longer wavelengths. The O^+ TOF spectra in Fig. 17 was obtained by excitation of the (1,1,0), (1,0,0), and (0,0,0)bands near 470 nm; the P(E) is shown in Fig. 18. Although weak $OCIO(A^2A_2)$ fluorescence has been previously observed^{25,26} in this wavelength region, photodissociation is known to occur on the picosecond time scale.²³⁻²⁷ This, combined with our observation of strong ClO+O signal with negligible production of Cl+O₂ shows that ClO+O is dominant even for the vibrationless (0,0,0) level. Owing to the relatively small absorption cross sections and small Cl yields near the $A^{2}A_{2}$ band origin, we have not attempted to study the Cl+O₂ channel near 470 nm.

TABLE I. CIO vibrational state distributions from various OCIO levels.

Band			F	F	ClO vibrational populations (% in v')						
ν_1	ν_2	ν_3	(cm^{-1})	(cm^{-1})	0	1	2	3	4	5	$\langle f_v \rangle$
0	0	0	21 016	372	100						0.00
1	0	0	21 724	1080	60	40					0.31
1	1	0	22 007	1363	50	50	•••				0.31
2	0	0	22 423	1779	38	62	•••				0.29
2	1	0	22 704	2060	24	51	25				0.41
3	0	0	23 117	2473	39	33	25	3			0.31
2	0	2	23 280	2636	13	47	37	3			0.26
3	1	0	23 393	2750	17	52	28	3			0.36
4	0	0	23 804	3160	21	17	46	16			0.42
3	0	2	23 958	3314	17	49	22	12			0.33
4	1	0	24 077	3433	11	28	37	21	4		0.44
3	1	2	24 225	3581	11	23	36	15	15		0.47
5	0	0	24 486	3842	23	16	24	25	12		0.41
4	0	2	24 633	3989	34	36	10	15	5		0.25
5	1	0	24 754	4110	17	24	25	13	20		0.39
4	1	2	24 896	4252	36	18	18	11	16		0.30
6	0	0	25 162	4518	42	22	12	10	14		0.24
5	0	2	25 304	4660	50	29	4	6	10		0.17
6	1	0	25 425	4781	25	21	21	15	17	1	0.32
5	1	2	25 564	4920	43	32	4	10	11		0.19
7	0	0	25 832	5188	26	42	12	6	10	4	0.23
6	0	2	25 970	5326	17	45	16	9	6	6	0.24
7	1	0	26 093	5449	17	37	20	8	7	11	0.28
6	1	2	26 229	5585	15	38	24	10	6	7	0.26
8	0	0	26 497	5853	14	46	16	12	12		0.23

TABLE II. CIO vibrational state distributions and Cl yields from various OCIO levels.

Band			ClO vibrational populations (% in v')							
ν_1	ν_2	ν_3	0	1	2	3	4	5	$\langle f_v \rangle$	Cl (%)
0	0	0	100						0.00	
1	0	0	60	40		•••	•••		0.31	
2	0	0	38	62		•••	•••		0.29	1.8
3	0	0	39	33	25	3	•••		0.31	2.9
4	0	0	21	17	46	16	•••		0.42	0.9
5	0	0	23	16	24	25	12		0.41	3.2
6	0	0	42	22	12	10	14		0.24	2.0
7	0	0	26	42	12	6	10	4	0.23	0.6
8	0	0	14	46	16	12	12		0.23	0.6
1	1	0	50	50					0.31	
2	1	0	24	51	25				0.41	1.0
3	1	0	17	52	28	3			0.36	2.6
4	1	0	11	28	37	21	4		0.44	2.1
5	1	0	17	24	25	13	20		0.39	3.9
6	1	0	25	21	21	15	17	1	0.32	2.4
7	1	0	17	37	20	8	7	11	0.28	1.4
2	0	2	13	47	37	3			0.26	1.0
3	0	2	17	49	22	12	•••		0.33	1.3
4	0	2	34	36	10	15	5		0.25	0.4
5	0	2	50	29	4	6	10		0.17	1.3
6	0	2	17	45	16	9	6	6	0.24	0.5
3	1	2	11	23	36	15	15		0.47	2.5
4	1	2	36	18	18	11	16		0.30	1.0
5	1	2	43	32	4	10	11		0.19	1.3
6	1	2	15	38	24	10	6	7	0.26	1.1



FIG. 14. O^+ TOF recorded at 40° for OClO absorption peaks near 410 nm.

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FIG. 15. Translational energy distributions for $O({}^{3}P)+CIO$ channel from $A {}^{2}A_{2}$ (4,0,0), (3,0,2), (4,1,0), and (3,1,2) levels.

E. Determination of $D_0(O-CIO)$

Provided that at least some of the ClO photofragments are formed in their ground rovibrational states and that some ground state $O({}^{3}P_{2})$ is produced, by measuring the maximum translational energy at a well defined excitation energy we obtain a strict upper limit for $D_{0}(O-ClO)$.⁵⁸ Substituting $E_{int,OClO} \sim 0$ into Eq. (3), and assuming that the fastest products correspond to production of internally cold $ClO({}^{2}\Pi_{3/2})+O({}^{3}P_{2})$:

$$D_0(O-ClO) = E_{\text{photon}} - E_{\text{trans,max,ClO+O}}.$$
(9)

Since OCIO A ${}^{2}A_{2}$ (0,0,0) lies only very slightly above $D_{0}(O-CIO)$, the maximum measured CIO+O translational energy release from this level should correspond to production of internally cold CIO+O, facilitating an absolute determination of $D_{0}(O-CIO)$. Using Eq. (9), $D_{0}(O-CIO)$ was consistently calculated to be 59.0±0.2 kcal/mol for decay of OCIO vibrational levels ranging from 1 to 13 kcal/mol above $D_{0}(O-CIO)$. Since the thermochemistry of the CIO and O are very well established,^{28,69} we can calculate the standard enthalpy of formation for OCIO at 0 K. According to the JANAF tables,²⁸ $\Delta H_{f}^{\circ}(CI) = 119.621 \pm 0.006$ kJ/mol (0 K) and $\Delta H_{f}^{\circ}(O) = 246.79 \pm 0.10$ kJ/mol (0 K). Spectroscopic studies on the CIO radical⁶⁹ led to a value for $D_{0}(CI-O)=265.38\pm0.033$ kJ/mol, and so $\Delta H_{f}^{\circ}(CIO) = 101.03 \pm 0.14$ kJ/mol (0 K). Using our value for



FIG. 16. Cl⁺ TOF recorded at 20° for OClO absorption peaks near 410 nm.

 $D_0(O-ClO)$, $\Delta H_f^\circ(OClO)$ (0 K)=100.9±1.0 kJ/mol (24.12 ±0.24 kcal/mol) and using the heat capacity correction from the JANAF tables,²⁸ $\Delta H_f^\circ(OClO)$ (298 K)=98.43±1.0 kJ/ mol (23.53±0.24 kcal/mol). Our result is in good agreement with a recent determination⁷⁰ of $\Delta H_f^\circ(OClO)$ (298 K)=96.65 ±4.18 kJ/mol, but considerably reduces the uncertainty.

Using $D_0(O-O)$, $D_0(Cl-OO)$, $D_0(ClO)$, and $D_0(O$



FIG. 17. O⁺ TOF recorded at 20° for OCIO absorption peaks near 470 nm.



FIG. 18. ClO+O translational energy distributions for OClO vibrational levels near 470 nm.

–ClO), the enthalpy of isomerization [reaction (10)] may be computed

$$OClO(X {}^{2}B_{1}) \rightarrow ClOO(X {}^{2}A'),$$

$$\Delta H(0 K) = -0.30 \pm 0.25 \text{ kcal/mol.}$$
(10)

Although the enthalpies of formation of the two isomers are nearly identical, they are separated by a large potential energy barrier.⁴⁴

F. Photodissociation at λ <400 nm

In Fig. 19, the O^+ TOF spectra (30°) for the cluster of peaks near 395 nm are shown. The slow contribution in the O^+ TOF data near 300 μ s results from fragmentation of the ClO product to O^+ in the ionizer. Note that the O^+ TOF spectra are very similar for all initial OCIO vibrational levels; i.e., the ClO vibrational energy distributions are not as strongly dependent on OCIO vibrational mode as was the case at lower excitation energies. The translational energy distributions for the ClO+O channel is shown in Fig. 20. Note that the ClO vibrational distributions for all levels except (6,1,0) are much colder than at longer wavelengths, with the dominant ClO vibrational level now v''=0,1 with a large translational energy release. Indeed, the fraction of excess energy channeled into ClO vibration decreases sharply from 0.41 for the (5,0,0) level to 0.21 for OCIO (6,0,0). (Tables I and II) Apparently, the ClO products become vibrationally cold with dominant production of v = 0 and v = 1 at wavelengths shorter than 390 nm. In addition, the relative contribution from the Cl+O₂ channel begins to diminish. For example, upon tuning from the (5,0,0) level to (6,0,0), the Cl yield decreases from 3.2% to 2.0%. Similarly, the yield decreases from 3.9% to 2.4% upon tuning from (5,1,0) to



FIG. 19. O⁺ TOF recorded at 30° for OCIO absorption peaks near 395 nm. Slower peak near $t=280 \ \mu s$ results from fragmentation of CIO to O⁺ in ionizer.

(6,1,0). These general trends continue as the excitation energy is further increased. As can be seen in Fig. 21, the $Cl+O_2$ channel is only barely observable from OCIO vibrational levels near 375 nm, even in the expanded figures.

G. Polarization dependence studies

The polarization angular dependence for the O atom products from the ClO+O channel is shown in Fig. 22 for a range of OClO(A^2A_2) vibrational levels. The CM product angular distribution is given^{62,63} by

$$f(\theta) = (1/4\pi)[1 + \beta P_2(\cos \theta)], \qquad (11)$$

where $P_2(\cos \theta)$ is the second order Legendre polynomial in cos θ . In Eq. (11), β can range from 2.0 for a purely parallel dissociation to -1.0 for a perpendicular process, and $\beta=0$ indicates an isotropic CM angular distribution. The ClO+O product polarization angular distributions were nearly isotropic ($\beta\sim0$) at wavelengths longer than 400 nm for OClO vibrational levels having zero quanta of asymmetric stretching. For example, the (5,0,0) angular distribution is isotropic to within the signal to noise ratio. The angular distribution recorded for the neighboring (4,0,2) level, however, is slightly anisotropic, with $\beta\sim0.1$.

We have not carried out a detailed study of the polarization dependence for the ClO+O channel over a wide range of wavelengths since, as explained below (Sec. IV C), most of the polarization dependence is washed out due to the relatively long dissociation time scales and strongly bent OClO



FIG. 20. ClO+O translational energy distribution for ClO+O channel from indicated A^2A_2 levels.

geometry. However, a few conclusions are obvious from the polarization measurements for the ClO+O channel shown in Fig. 22: (i) We always observe positive values for β , consistent with the parallel polarized nature of the $(A \ ^2A_2 \leftarrow X \ ^2B_1)$ electronic transition. (ii) β steadily increases upon tuning to the blue but remains much less than the limiting value of 2.0 even at 360 nm. (iii) For a given excitation energy, dissociation of OClO($A \ ^2A_2$) combination bands having asymmetric stretching excitation leads to more anisotropic ClO+O angular distributions than those associated with pure symmetric stretching.

We looked for a polarization dependence of the Cl products from the Cl+O₂ channel at wavelengths near 400 nm where it contributed most strongly and therefore provided the highest signal to noise ratio. However, no dependence of the Cl product intensity on polarization angle was observed to within the signal to noise ratio of the experiment. Consequently, $\beta = 0$ (an isotropic angular distribution) was assumed in analyzing the $Cl+O_2$ data at all wavelengths. At shorter wavelengths (near 380 nm), where the OCIO lifetimes are decreasing (as evidenced by more strongly anisotropic ClO+O distributions), the $Cl+O_2$ yield became very small. Although no polarization dependence of the $Cl+O_2$ signal was observed, due to the very weak signal level a slightly anisotropic distribution would have been undetectable in our experiment. Furthermore, in order to obtain good signal to noise ratios without prohibitively long data accu-



FIG. 21. Cl^+ TOF spectra (30°) for OClO peaks near 380 nm showing absence of Cl+O2 channel.

mulation times, relatively high laser powers (>1 mJ) were required. Under such conditions, saturation effects could diminish any small anisotropy present in the $Cl+O_2$ angular distribution.

If the Cl+O₂ distribution was actually slightly anisotropic at $\lambda < 400$ nm, our assumption that $\beta = 0$ would have led to a small error in our determination of the Cl:ClO branching ratios. Most of the experimental data was recorded using a vertically polarized laser beam, with the direction of the electric vector perpendicular to the axis of the detector. Assuming that Cl+O2 results from concerted unimolecular dissociation of OCIO from a near- C_{2v} transition state (i.e., from a symmetric transition state having a compressed OCIO bond angle), the Cl+O₂ products are most likely to recoil preferentially along the C_{2v} axis. Since the direction of the $(A^{2}A_{2} \leftarrow X^{2}B_{1})$ transition dipole is perpendicular to the C_{2v} axis, an anisotropic Cl+O₂ CM angular distribution would peak perpendicular to the polarization angle ($\beta < 0$), leading to an enhanced signal level near the axis of the detector. Thus, if the $Cl+O_2$ angular distribution was slightly anisotropic, our assumption that $\beta = 0$ would have led to a small overestimate of the Cl:ClO branching ratio. However, in view of the long dissociation timescales where the $Cl+O_2$ channel is operative, we believe that the magnitude of any such error would be considerably smaller than the stated 20% error limit.

H. CIO and CI TOF spectra near 360 nm

We have examined the dissociation dynamics near 360 nm in considerable detail. In particular, we looked for the



FIG. 22. Dependence of ClO+O channel (monitored at O^+) to laser polarization angle for various A^2A_2 vibrational levels.

 $Cl+O_2$ channel first discussed by Vaida *et al.*³⁹ and subsequently described by Bishenden and Donaldson.^{52,53} The Cl vield reported by the latter workers range from a lower limit of a few percent to as high as 15%. The ClO and Cl TOF spectra, obtained at 30° for the (10,0,0) band at 360 nm are shown in Fig. 23. The dye laser beam was vertically polarized, 3 mm diam., and 1 mJ/pulse. The dominant features at $t = 200-600 \ \mu s$ have the same shape, and are identical after accounting for the slightly different transmission times of the two different masses through the mass filter. The Cl TOF corresponds to the Cl⁺ daughter ions resulting from fragmentation of CIO (produced from the CIO+O channel) upon electron impact ionization. In the inset to the Cl TOF spectrum in Fig. 23, the vertical axis is expanded by a factor of 100 to enhance the region where Cl+O₂ channel is most likely to be observed. The solid line in the inset in Fig. 23 is the calculated TOF assuming a yield of 0.2% for Cl+O₂ production, using the Cl+O₂ P(E) determined at 404 nm, and that shown in Fig. 24 for the ClO+O channel. Since the observed contribution lies below the solid line, the Cl+O₂ product channel that we observed near 404 nm cannot account for more than 0.2% in this wavelength region.



FIG. 23. TOF spectra for CIO and Cl resulting from excitation to the (10,0,0) peak near 360 nm. Dominant Cl⁺ peak is daughter ion from fragmentation of CIO in electron impact ionizer detector. Inset: Vertical scale expanded by factor of 100. Solid line in the inset is calculated contribution assuming 0.2% yield of Cl+O₂.

As shown in the inset in Fig. 23 (solid points), some very weak fast Cl signal appears to be present near T = 100-130 μ s, lying below our upper limit of 0.2%. However, the power dependence studies shown in Fig. 25 suggest that this fast contribution results primarily from a multiphoton effect. The dominant, broad feature in the Cl TOF spectra, peaking at $t = 255 \ \mu s$, maintains constant shape with increasing laser pulse energy. Since this dominant contribution depended linearly on laser pulse energy (up to ~2.5 mJ/pulse), it corresponds to a single photon process. At pulse energies above 2.5 mJ, the general shape of this dominant contribution remained nearly constant, even though we calculated (using the known absorption cross sections) that the $(A^{2}A_{2} \leftarrow X^{2}B_{1})$ transition must be strongly saturated. In the insets to Fig. 25, the solid line corresponds to the calculated contribution for the Cl+O₂ channel assuming a yield of 0.2%. Since our experimental data (solid points) shows that the contribution from the faster component *increases* relative to the dominant 255 μ s peak at higher pulse energies, it must



FIG. 24. ClO+O translational energy distribution [P(E)] for products from decomposition of (10,0,0) vibrational level prepared by excitation at 360 nm.



FIG. 25. Cl TOF spectra from decay of (10,0,0) vibrational level recorded at various laser pulse energies. Shape of dominant contribution (t=220-700 μ s) is independent of energy (one photon process). Fast contribution (t=100-200 μ s) increases at higher pulse energy (multiphoton process). Solid line corresponds to upper limit of 0.2% for Cl+O₂ channel, determined at 1 mJ/pulse.

result from a multiphoton process; likely photodissociation of vibrationally excited ClO by a 360 nm photon. The data obtained at 1 mJ/pulse (Figs. 24 and 25) indicates that the upper limit to the Cl+O₂ yield is 0.2%. We have not attempted to reduce this limit further due to the decreased signal to noise ratio at smaller laser pulse energies and the expectation that an upper limit of 0.2% for the Cl+O₂ channel already renders it insignificant from an atmospheric standpoint. As discussed below, polarization dependence studies failed to turn up any evidence for production of Cl+O₂ at other polarization angles.

We have considered the possibility that a channel producing Cl+O₂ near 360 nm might involve a different reaction mechanism than at the longer wavelengths, possibly producing highly internally excited O2. If this were the case, less energy would be available for Cl+O₂ translational energy and these products might be constrained to angles within 30° of the OClO molecular beam and would not appear in Figs. 23 or 25. To investigate this possibility, we have recorded the CIO and Cl TOF spectrum at an angle of 13° from the molecular beam, as shown in Fig. 26. Again, the solid line is the calculated TOF using the P(E), in Fig. 24. If $Cl+O_2$ was formed with low CM translational energy release, their laboratory velocities (v) would be comparable to the OClO beam velocity (\sim 1260 m/s), and would appear at $T \sim 315 \ \mu s$. Although our ability to detect products formed with low CM velocities (u) is considerably enhanced by the v^2/u^2 factor in the CM \rightarrow LAB product intensity transformation, no significant Cl⁺ contribution was observed in excess



FIG. 26. CIO and CI TOF spectra recorded at 13° for decay of (10,0,0) vibrational level. TOF spectra are identical, with no contribution observed for Cl+O₂ channel.

of that expected from fragmentation of ClO in the ionizer.

It is appropriate to consider whether or not it is possible for Cl+O2 to be constrained to beam-detector angles even smaller than 13°, and still remain undetected in our experiment. At 360 nm, the excess energy available to the $Cl+O_2$ products from OCIO photodissociation is $26,100 \text{ cm}^{-1}$ $(\sim 74.5 \text{ kcal/mol})$. For Cl+O₂ products to escape detection at 13° would require that they be formed with $E_{\text{trans}} < 0.7 \text{ kcal}/$ mol. For the $Cl({}^{2}P_{3/2}) + O_2$ channel, translational energies below 0.7 kcal/mol would require that the O₂ be formed with 73.8-74.5 kcal/mol of internal excitation, implying exclusive production of $O_2(X^{3}\Sigma_{g}^{-}, v=19, J=24-30)$, $O_2(a^{-1}\Delta_{g}, v=13, J>39)$, $O_2(a^{-1}\Delta_{g}, v=14, J=0-10)$, $O_2(b^{-1}\Sigma_{g}^{+}, v=9, J>40)$ or $O_2(b^{-1}\Sigma_{g}^{+}, v=10, J=0-11)$.^{28,29} We believe that such narrow O_2 rovibrational state distributions, peaking within 0.7 kcal/mol of the maximum available energy, is exceedingly unlikely. Therefore, Cl+O₂, if produced, could not escape detection in our experiment because of insufficient recoil energy. There has been considerable reference in the literature to "photochemical isomerization" of OCIO to CIOO following electronic excitation of OCIO near 360 nm.38-41 Under collisionless conditions in the gas phase, if the ClOO isomer (D_0 Cl-OO=4.5 kcal/mol) were formed, it would rapidly dissociate to Cl+O₂ or isomerize back to OCIO and decay to CIO+O. Radiative processes are too slow for appreciable production of bound ClOO in the gas phase.

The polarization angular dependence observed for the Cl⁺ resulting from decomposition of OCIO (10,0,0) prepared at 360 nm was shown in Fig. 22. The solid line fit to the data indicates β =0.2±0.1. A positive value for β is consistent with the parallel nature of the OCIO($A^2A_2 \leftarrow X^2B_1$) transition which is believed to carry all of the oscillator strength in this wavelength region.^{21,45} The polarization dependence of the Cl⁺ TOF spectra from OCIO(10,0,0) was also found to be consistent with β =0.2±0.1, as expected since the signal results exclusively from fragmentation of ClO to Cl⁺ in the ionizer. As shown in Fig. 27, the shapes of the Cl TOF



FIG. 27. Cl TOF spectra at various laser polarization angles, $\theta_p \cdot \theta_p = 0^{\circ}$ corresponds to laser polarization along the detector axis. $\theta_p = 90^{\circ}$ corresponds to vertical laser polarization. Shape of TOF spectra is nearly the same for each polarization angle with no evidence for Cl+O₂ channel.

spectra recorded at various laser polarization angles remained nearly constant and no additional components attributable to $Cl+O_2$ production was observed at any polarization angle for OCIO (10,0,0).

In Fig. 28, the time of flight distributions for O atoms from the ClO+O channel is shown for neighboring OClO vibrational levels near 370 nm. Note that there are considerable differences in the shapes of these TOF spectra. The CIO+O internal state distributions are thus *mode specific*, albeit less so than at wavelengths near 400 nm. The translational energy distributions derived from this data are shown in Fig. 29. In all four spectra, the translational energy distributions P(E) peak near 13 kcal/mol, indicating that a large fraction of the excess energy appears in ClO+O translational energy release. This behavior contrasts that for wavelengths near 400 nm where a relatively large fraction of excess energy appears as ClO vibrational energy, with most thermodynamically accessible ClO levels populated. As shown in Figs. 30 and 31, near 360 nm the ClO is also produced in low vibrational levels (v = 1-3), with very little contribution for $v \ge 4$ ($E_{\text{trans}} < 10$ kcal/mol). In the translational energy distributions shown in Figs. 29 and 31, we have normalized the P(E) distributions for neighboring levels to unit area since (as discussed below), $\phi_{\text{CIO+O}}$ >0.998. A notable observation in Fig. 29 is that the ClO internal state distribution from OCIO (8,0,2) is narrower than the others, peaking more sharply at 13.5 kcal/mol, with P(E) reaching 0.23. However, for all of the neighboring OCIO vibrational levels shown in Fig. 29, the P(E) remains well below 0.20. As shown in



FIG. 28. O⁺ TOF spectra (60°) from indicated A ${}^{2}A_{2}$ vibrational levels near 370 nm. Note that the shapes for different vibrational levels are different, with narrowest TOF for ${}^{2}A_{2}$ (8,0,2).

Figs. 30 and 31, we observed analogous behavior for the absorption peaks near 360 nm, with the (9,0,2) level leading to a more sharply peaking translational energy distribution. We conclude that at 360-370 nm, asymmetric stretching excitation in the initially prepared A^2A_2 levels leads to narrower ClO rovibrational energy distributions.

IV. DISCUSSION

A. Dynamics at λ >380 nm

Due to a substantial potential energy barrier for dissociation of the "bright" A^2A_2 surface to ClO+O (Fig. 3⁴³) along the asymmetric stretching coordinate, the photodissociation of OCIO at E < 3.1 eV must be indirect, involving interactions with one or more lower lying states.⁴³ The narrow linewidths of the absorption features in this energy region indicates that dissociation time scales are many picoseconds.^{21–27} This long decay lifetime, combined with substantial bending of the parent OCIO molecule (see below) leads to product angular distributions which are nearly isotropic (β =0).

Detailed linewidth studies by McDonald and Innes,²³ and later by Michielsen *et al.*²² showed that decay lifetimes are independent of rotational level but dissociation of the F_1 spin component $(J=N+\frac{1}{2})$ is approximately twice as fast as that for F_2 $(J=N-\frac{1}{2})$. It was argued²³ that the ground X^2B_1 electronic state was unlikely to be the perturber because even



FIG. 29. Translational energy distributions P(E) for ClO+O channel indicated A^2A_2 vibrational levels pumped near 370 nm, normalized to unit area. Mode specific ClO vibrational distributions are evident with enhanced contribution for $E_{\text{trans}} \sim 13$ kcal/mol from the (8,0,2) level.



FIG. 30. O⁺ TOF spectra (60°) from indicated OCIO vibrational levels near 360 nm. Note that the shapes for different vibrational levels are different, with narrowest TOF for $A^{-2}A_{2}$ (9,0,2).



FIG. 31. Translational energy distributions P(E) for ClO+O channel from indicated A^2A_2 vibrational levels pumped near 360 nm, normalized to unit area. Mode specific ClO vibrational distributions are evident with enhanced contribution for $E_{\text{trans}} \sim 14$ kcal/mol from the (9,0,2) level.

near the A^2A_2 (0,0,0) origin, the X^2B_1 level density would be high and this should tend to smooth out any dependence of linewidth on spin component. It was concluded that the dissociation mechanism involves spin–orbit interactions between the A^2A_2 and the nearby 2B_2 or 2A_1 states. The insensitivity of linewidth on OCIO rotational level,^{22,23} was taken as evidence that the perturbing levels have nuclear geometries similar to the A^2A_2 .

Analysis of high resolution spectra near the A^2A_2 band origin showed that the linewidths associated with bending (ν_2) were more than twice as broad as pure symmetric stretching. However, linewidths were independent of symmetric stretching level (ν_1) for $\nu_1=0-3$.^{22,23} The optically prepared A^2A_2 and the nearby 2B_2 form a Renner–Teller pair, becoming orbitally degenerate $({}^2\Pi_g)$ in their linear configurations. Since interactions between Renner–Teller pairs are expected to be enhanced by bending, the 2B_2 was favored as the spin–orbit perturber in the early studies.^{22,23} However, the recent *ab initio* calculations⁴³ indicate that the 2B_2 interacts directly with the A^2A_2 only at considerably higher energies, whereas the 2A_1 crosses the A^2A_2 near the A^2A_2 equilibrium angle. It was thus concluded⁴³ that the 2A_1 is the spin–orbit perturber of the A^2A_2 .

As shown in Fig. 3, Peterson and Werner's calculations⁴³ show that the ${}^{2}A_{1}$, like the $A {}^{2}A_{2}$, is bound at E < 3.1 eV with respect to dissociation to ClO+O along the asymmetric stretching coordinate for bond angles near equilibrium (100°). However, those theoretical calculations (see Fig. 3) indicated the existence of a very small barrier to

linear OCIO along the ${}^{2}A_{1}$ bending coordinate, with the energy of linear OCIO lying lower than the bent form. The height of the barrier to achieve linearity (for fixed OClO bond length) appeared to lie very close to the energy of the $A^{2}A_{2}$ origin (~2.8 eV).⁴³ The calculations indicated that dissociation to ClO+O can subsequently proceed via a nearly linear ${}^{2}A_{1}$ transition state with the height of the barrier for dissociation estimated to be lower than that to achieve linearity. Our results are consistent with these conclusions. Our finding that ClO+O production is by far the dominant channel for all $A^{2}A_{2}$ levels down to the (0,0,0) level confirms that the ${}^{2}A_{1}$ lies below A ${}^{2}A_{2}$ (0,0,0). Furthermore, our observation of strong ClO+O signal even from OCIO (0,0,0) indicates that interactions between the ${}^{2}A_{1}$ and $A^{2}A_{2}$ are significant in the region of the $A^{2}A_{2}$ origin, consistent with a crossing between these levels near the $A^{2}A_{2}$ minimum.

At excitation energies below 3.1 eV (λ >400 nm), the CIO is formed vibrationally excited with large populations of nearly all thermodynamically accessible vibrational levels. The width of each vibrational peak in the TOF spectra is a convolution of the ClO rotational and spin orbit distribution, and is further broadened by the distribution of $O({}^{3}P)$ spinorbit levels. The ClO(X ${}^{2}\Pi_{1/2,3/2}$) spin-orbit levels are separated by 350 cm⁻¹ and the excited spin-orbit $O({}^{3}P_{I})$ levels lie at 158 cm⁻¹ (J=1) and 227 cm⁻¹ (J=0). Since we are unable to resolve these fine structure levels, the ClO rotational distributions cannot be obtained from the widths of the vibrational envelopes for the ClO+O P(E). However, from the fact that each vibrational contour peaks well away from the maximum theoretical translational energy, it is clear that the ClO rotational distributions peak well away from J''=0. Because the ClO vibrational spacing (~2.4 cm⁻¹ at low v'') is clearly well resolved in our TOF data, the ClO rotational envelopes must be considerably narrower than the 350 cm^{-1} vibrational spacing. We thus conclude that at excitation wavelengths longer than 400 nm, the ClO products are formed vibrationally hot with only a modest degree of rotational excitation.

Michielsen and co-workers found that decay lifetimes at $\nu_1 = 0-3$ were independent of symmetric stretching level (ν_1) ²² Their additional finding that OCIO predissociation rates are enhanced by parent bending is clearly important to unravelling the dynamics in the low energy region. Peterson and Werner⁴³ compared one dimensional cuts of the symmetric stretching potentials for the four OCIO electronic states at fixed angles of 106.4° and 117.4°, corresponding to the equilibrium bond angles for the prepared A^2A_2 and ground ${}^{2}B_{1}$ state, respectively. They noted that OCIO bending has a strong effect on the energies of the $A^2 A_2/^2 A_1$ crossings, consistent with the observation that OCIO decay lifetimes are diminished with bending excitation. An additional reason for the enhancement seen with parent bending is that initial $A^{2}A_{2}$ bending provides nuclear motion facilitating increased access to regions of the ${}^{2}A_{1}$ surface favorable to decay to CIO+O. As noted above, this corresponds to nearly linear nuclear configurations where the potential energy barrier is lowest. Our observation of highly vibrationally excited ClO with modest rotational excitation in this low energy region of the OCIO absorption spectrum appears to support the hypothesis that a large fraction of the CIO+O products originate from a nearly linear $OCIO(^2A_1)$ transition state.

As noted in the results section, the P(E) for the Cl+O₂ channel is bimodal (Fig. 7). From energy conservation, the fastest component, lying in the energy range 41-67 kcal/ mol, must correspond to production of ground state O2 $X^{3}\Sigma_{p}^{-}$ in vibrational levels ranging from v''=1-6. The rise near E=41 kcal/mol corresponds exactly to the expected maximum translational energy release for O₂ $a^{-1}\Delta_g$ (v''=0) or $O_2 X^{3}\Sigma_{g}^{-}$ (v''=6). Since it seems unlikely that the $O_2(X^{3}\Sigma_g^{-})$ vibrational energy distribution would be so bimodal and highly inverted to rise sharply above v=6, we attribute the rise below E=41 kcal/mol to formation of O_2 $a^{-1}\Delta_g$ (v''=0). We conclude that approximately 20% of the O_2 is ground state $(X^{3}\Sigma_{g}^{-})$ formed in vibrational levels between 0 and 5. From the sharp rise below 41 kcal/mol, the dominant O₂ products are in the electronically excited $a^{-1}\Delta_{\sigma}$ state. The exact location of this peak indicates that the $O_2(a^{-1}\Delta_a)$ is primarily formed in v''=0-4. Note that the maximum in the P(E) for the Cl+O₂ channel lies at 32 kcal/mol, slightly higher than the maximum allowed translational energy release for production of $\text{Cl}+\text{O}_2(b^{-1}\Sigma_g^+)$, ruling out the possibility that the sharp rise corresponds to these products. Of course, some contribution from this channel may be hidden under the dominant $Cl+O_2(a^{-1}\Delta_a)$ peak at slightly lower translational energies.

Owing to the presence of a conical intersection between the ${}^{2}A_{1}$ and ${}^{2}B_{2}$ states near the minimum in the ${}^{2}A_{1}$ bending potential, vibronic interactions mediated by b_2 asymmetric stretching should be appreciable.⁴³ The ${}^{2}B_{2}$ electronic state is an optically dark level, not accessible by a direct dipole transition from the ground state. As discussed elsewhere,⁴²⁻⁴⁴ all available evidence indicates that Cl+O₂ production primarily involves decomposition from ${}^{2}B_{2}$ levels. Due to the O=O bonding and Cl-O antibonding character of the b_2 orbital, the 2B_2 is strongly bent with an equilibrium OCIO angle of ~90°.⁴³ In C_{2v} symmetry, $OClO(^{2}B_{2})$ correlates to $Cl(^{2}P) + O_{2}(a^{-1}\Delta_{g})$, consistent with our finding that $a^{-1}\Delta_g$ is the dominant electronic state of the O₂ products. However, the 20% yield of O₂($X^{3}\Sigma_{\rho}^{-}$) observed in our experiment indicates that C_{2v} symmetry is broken to some degree, facilitating a crossing to the ground electronic state as the products separate.

An interesting observation is that the O₂ translational energy distributions were essentially identical for many A^2A_2 levels. For example, we were able to fit the Cl+O₂ distributions from the (5,0,0), (4,0,2), and (5,1,0) levels with the same P(E). This relative insensitivity to initial vibrational state suggests that the O₂ state distributions are primarily determined rather late in the decomposition process, as the Cl+O₂ are departing. However, a survey of the Cl TOF spectra over a wider range of excitation wavelengths does reveal some interesting effects. As can be seen in Fig. 16, for example, at slightly lower energies near the (4,1,0), the relative contribution from the slower, $O_2(a^{-1}\Delta_g)$ channel is nearly the same as the faster $O_2(X^{-3}\Sigma_g^{-1})$ peak. Thus the yield of electronically excited $O_2(a^{-1}\Delta_g)$ relative to the ground state diminishes as the excitation energy is decreased towards that of the potential energy barrier for this channel. This is predicted by the theoretical calculations.⁴⁴ As discussed by Peterson and Werner, the potential energy barrier for Cl+O₂ production on the 2B_2 surface is strongly dependent on OCIO geometry, with substantial decrease in the barrier height for non- C_{2v} geometries.⁴⁴ The relative contribution of ground state $O_2(X \, {}^3\Sigma_g^-)$ therefore increases upon decreasing the excitation energy towards the top of the potential energy barrier as a larger fraction of products result from non- C_{2v} trajectories.

The possibility that OCIO symmetric bending might lead to a dramatic enhancement in Cl+O2 production rates has been raised^{21(b)} in connection with the atmospheric significance of OCIO photochemistry. It was suggested that the absence of $A^{2}A_{2}$ peaks associated with two quanta of bending (e.g., 5,2,0) might be attributable to extreme broadening of those peaks due to very short lifetimes resulting from rapid decomposition to Cl+O2. We have looked for enhanced Cl+O₂ production at the calculated band positions for A^2A_2 (5,2,0) and (4,2,0), but saw no evidence for significant $Cl+O_2$ at these wavelengths. This, along with our finding that ClO+O remained dominant for all OClO levels (including those with bending), shows that the Cl+O₂ channel is never greatly enhanced with A^2A_2 bending excitation. Thus the lack of activity for OCIO combination bands having two quanta of bending is more likely explained by symmetry effects operative in the three normal modes, as discussed qualitatively by Brand et al.⁷¹

The mode specific Cl:ClO branching ratios observed in this work are entirely consistent with the recent calculations by Peterson and Werner.⁴⁴ Although their calculations reveal the existence of a low-lying transition state for Cl+O₂ production on the strongly bent ${}^{2}B_{2}$ surface, a second transition state was also found, leading to production of ClO+O via the asymmetric stretching coordinate. It is thus not surprising that any asymmetric stretching excitation in the initially prepared A ${}^{2}A_{2}$ levels strongly diminishes Cl+O₂ production in favor of ClO+O. Clearly, the nuclear motion associated with the initially prepared OCIO vibrational modes plays a critical role in controlling the identity of the products. Only those ${}^{2}B_{2}$ levels very near C_{2v} reach Cl+O₂. Any asymmetric vibrational excitation strongly promotes decay to ClO+O, consistent with the shorter dissociation time scales and therefore, more strongly anisotropic angular distributions, as well as strongly diminished Cl+O₂ yields.

B. Change in dynamics near 400 nm

Upon tuning to wavelengths shorter than 400 nm, significant changes are observed in both product channels. Whereas most energetically accessible CIO vibrational energy levels are populated with strongly mode specific distributions at longer wavelengths, upon tuning to shorter wavelengths the CIO becomes vibrationally cold, with most excess energy channeled into relative translational energy. In this same energy region, the $Cl+O_2$ channel diminishes significantly. Interestingly, Richard and Vaida observed a considerable increase in the OCIO absorption linewidths above 3.1 eV.²¹ In particular, a plot of the absorption linewidths [Ref. 21(b) Fig. 3] shows a rapid increase from 0.3 cm⁻¹ for A^2A_2 (5,0,0) to ~0.9 cm⁻¹ for A^2A_2 (7,0,0).

All of the changes noted above clearly indicate the onset of a new ClO+O decomposition mechanism at E>3.1 eV. Our experimental observations and the theoretical calculations^{43,44} provide strong evidence that this change is associated with the opening of the ClO+O channel on the $A^{2}A_{2}$ surface. At energies above the barrier to ClO+O, the direct adiabatic coupling to the CIO+O continuum increases sharply, and dissociation time scales decrease. The photochemical dynamics and branching ratios are governed by the strength of the coupling of the prepared $A^{\bar{2}}A_2$ state to the available decay channels.^{43,44} As the reaction rate constant for dissociation to ClO+O on the bright A^2A_2 surface increases, the nonadiabatic behavior ultimately leading to Cl+O₂ production becomes negligible and so this channel closes. The large translational energy release and production of vibrationally cold CIO are signatures of the existence of a substantial potential energy barrier for ClO+O production with strong ClO-O repulsion in the exit channel. Our data indicates that ClO produced from OClO photodissociation near 360 nm is in low vibrational levels (v''=1-3), with negligible production of v'' > 4. This clearly disagrees with previous conclusions that the ClO is primarily formed in v''=4-6 in this wavelength region.^{39,40}

C. Polarization dependence studies

Photodissociation of OCIO near 360 nm leads to production of ClO+O with a translational energy distribution peaking near 13 kcal/mol (Fig. 31), corresponding to a most probable center of mass O atom velocity of 2360 m/s. The effect of the initial tangential velocity of the O atom due to OCIO parent rotation is thus negligible in the present case. However, β is reduced considerably from the maximum possible value of 2.0, primarily because the direction of O atom product recoil (along the Cl–O bond axis) does not lie along the axis of the transition dipole. OCIO is a strongly bent molecule with an equilibrium bond angle of 117.4° for the ground $X^{2}B_{1}$ state, and 106.2° for the excited $A^{2}A_{2}$ level.²¹ The OCIO (A ${}^{2}A_{2} \leftarrow X {}^{2}B_{1}$) transition moment lies parallel to the OCIO a axis, i.e., in the OCIO plane perpendicular to the C_{2v} axis. Thus the Cl–O bond axis, along which the O atom departs, lies 31°-37° from the direction of the transition dipole moment. The second factor which diminishes β is that the OCIO parent molecule has a dissociation lifetime of at least several hundred femtoseconds²¹⁻²⁷ so the parent molecule will undergo a fraction of a rotation before dissociating, as in NO₂ photodissociation.⁶³

The photofragment anisotropy parameter (β) is related to parent lifetime (τ) by the following expression:⁶³

$$\beta = 2P_2(\cos\chi) \left(\frac{1+\omega^2 \tau^2}{1+4\omega^2 \tau^2} \right). \tag{12}$$

In Eq. (12), χ is the angle between the recoil velocity vector of the fragment and the parent transition dipole moment, and ω is the frequency of parent rotation. Estimating T=15 K and using the moment of inertia for OClO, we calculate $\omega = 6.4 \times 10^{11} \text{ s}^{-1}$. The ground state OClO bond angle (θ =117.4°) corresponds to χ =31.3° and that of the excited state (θ =106.2°) corresponds to χ =36.9°. Upon substituting these values into Eq. (12), it is apparent that the large value of χ leads to substantial reduction in β . Indeed, even in the limit of $\tau=0$ (instantaneous dissociation), assuming dissociation from a ground state geometry ($\chi = 31.3^{\circ}$), the maximum value for β is 1.19. If the molecule dissociates from the excited state geometry ($\chi = 36.9^\circ$) the maximum in β is only 0.92. Thus because χ likely has a range of values as OCIO undergoes strong bending after excitation, it is impossible to reliably extract OCIO lifetime information from our anisotropy measurements using Eq. (12). However, if we assume that OCIO dissociates from a geometry close to that of the excited A ${}^{2}A_{2}$ state (106.2°), the following β values are calculated: $\beta = 0.72$ ($\tau = 500$ fs); $\beta = 0.49$ ($\tau = 1$ ps). Our observed value of 0.2±0.1 near 360 nm would be consistent with a dissociation time scale exceeding 1 ps for OCIO (10,0,0). As expected, this is somewhat longer than those measured directly by Zewail's group in experiments which were at considerably higher excitation energies ($\lambda < 350$ nm).55

D. Nature of the mode specificity near 360 nm

Following our report²⁰ of mode specific Cl:ClO yields near 400 nm, a similar effect was reported by BD near 360 nm.⁵³ Specifically, the enhanced CIO intensities from OCIO (8,0,2) and (9,0,2) was taken as evidence that the quantum yields for this channel are enhanced with OCIO asymmetric stretching excitation. Surprisingly, the Cl REMPI spectra resembled the OCIO absorption spectrum, leading those workers to conclude that the Cl+O2 yield was constant. This conclusion, if correct, together with conservation of product flux dictates the existence of another photochemical channel which *decreases* when OCIO asymmetric stretching levels are excited. However, since the following arguments lead to the conclusion that $\phi_{Cl+O_2} + \phi_{ClO+O} \ge 0.9998$ near 360 nm, no other photochemical channels can be significant: (i) The quantum yield for OClO(A^2A_2) fluorescence is negligible (i.e., $<2\times10^{-4}$) due to picosecond dissociation time scales.^{21–27} (ii) Formation of Cl+O+O is energetically closed.²⁸ (iii) The ClOO(²A") isomer ($D_0 = 4.5 \text{ kcal/mol}^{50}$), if produced, would be formed above D_0 and would rapidly dissociate to Cl+O₂. (iv) OClO(A^2A_2) levels excited near 360 nm lie above the barrier for dissociation to ClO+O. Other OCIO electronic states $({}^{2}A_{1}, {}^{2}B_{2}, \text{ or } X {}^{2}B_{1})$ are dissociative at these energies⁴³ so metastable or fluorescent OCIO levels cannot be significant. From these considerations, we conclude that >99.98% of the excitation events lead to $Cl+O_2$ or ClO+O. Since only two channels are operative, enhancement in the ClO+O yield must be accompanied by a decrease in Cl+O₂ production, independent of reaction mechanism(s). This is equivalent to saying that the partial absorption cross sections for the two competing channels must add to the total OCIO absorption cross section. Since this requirement is not fulfilled in Ref. 53, the claim of mode specific Cl:ClO branching ratios near 360 nm must be in error.

Flesch and co-workers⁵⁶ have carried out a photodissociation study of OCIO and its molecular aggregates. They detected ClO following OCIO photodissociation by single photon ionization at 10.91 eV, just above the adiabatic ClO ionization potential of 10.87 eV. They, like BD, observed enhanced ClO signal from OCIO vibrational modes having asymmetric stretching excitation (ν_1 ,0,2) near 360 nm. However, they attributed this behavior to different ClO vibrational energy distributions from each OCIO parent A^2A_2 vibrational level.⁵⁶ They postulated that since ClO ionization cross sections are likely to depend on vibrational level, the ClO detection sensitivities will not be constant for ClO products from different parent OCIO vibrational states.

Our work confirms that the CIO vibrational distributions from OCIO photodissociation at 360-370 nm are indeed mode specific. Most notably, the ClO translational energy distributions are narrower and more sharply peaking for OCIO asymmetric stretching levels than for neighboring peaks. The exact peak locations in the P(E) shown in Fig. 29 indicates that decay of OCIO (8,0,2) leads to enhanced production of $ClO(v''=2,J''<15\frac{1}{2})$ or $ClO(v''=1,J''>35\frac{1}{2})$, relative to neighboring OCIO absorption peaks. Similar behavior is seen for OClO (9,0,2), as shown in Fig. 31. Since there is no resolvable structure in the OClO (8,0,2) or (9,0,2)P(E)'s, and because the O(${}^{3}P_{I}$) spin-orbit distributions are unknown, we cannot distinguish between production of ClO v=1 and 2 from the P(E)'s shown in Figs. 29 and 31. However, it is clear from our data that if the most probable CIO levels are monitored state specifically (e.g., using 2+1REMPI) while scanning the OCIO excitation laser at 360-370 nm, the ClO signal will appear to be enhanced for OClO (8,0,2) and (9,0,2), relative to neighboring peaks. Such behavior results from the narrower P(E) and sharper peaking of the ClO rovibrational state distribution, rather than from increased ClO:Cl branching ratios.52,53 Since the ClO absorption cross section into the dissociative $A(^{2}\Pi)$ continuum^{72,73} should not vary significantly for ClO (v''=1-3), a constant fraction of CIO products are photolyzed by the 235 nm probe laser producing a Cl REMPI spectrum which follows the OCIO absorption spectrum, as reported in Ref. 53.

V. CONCLUSIONS

We have studied the photodissociation of OCIO using photofragment translational energy spectroscopy and have obtained branching ratios for the two photochemical channels over a wide range of wavelengths. The dominant channel (\geq 96%) is production of CIO+O. Although the vibrational distributions of the CIO product are strongly dependent on the initial OCIO vibrational level, at λ >400 nm essentially all thermodynamically accessible vibrational levels are produced. The preferential formation of vibrationally excited CIO is rationalized in terms of the recent *ab*

J. Chem. Phys., Vol. 105, No. 18, 8 November 1996. This article is copyrighted as indicated in the article. Reuse of AIP content is subject to the return of the *initio* calculations which indicated that the bright A^2A_2 state is bound with respect to dissociation at E < 3.1 eV but interacts via spin orbit coupling to a nearby 2A_1 which dissociates to ClO+O via a nearly linear transition state. The Cl+O₂ channel, which to date has received considerable attention due to its potential for atmospheric ozone depletion, was clearly observed but plays only a minor role. As expected from orbital symmetry considerations, the O₂ was primarily formed in the $a^{-1}\Delta_g$ state, suggesting that the mechanism involves concerted decomposition from an OCIO transition state near C_{2v} symmetry.

Our finding that the Cl:ClO branching ratios are enhanced slightly with bending excitation but strongly diminished with asymmetric excitation in the initially prepared A^2A_2 levels is entirely consistent with the recent *ab initio* calculations by Peterson and Werner which revealed the existence of two transition states for dissociation on the dark strongly bent 2B_2 surface.⁴⁴ Although one relatively low energy transition state led to production of Cl+O₂ along the symmetric bending coordinate, a second lower frequency transition state led to ClO+O via asymmetric stretching. Any asymmetric motion in OClO 2B_2 is thus expected to strongly enhance dissociation to ClO+O, thereby diminishing the yield of Cl+O₂.

At excitation energies above 3.1 eV (λ <400 nm), the Cl+O₂ channel was found to diminish strongly with the ClO+O yield reaching approximately unity at λ <380 nm. This observation, combined with the sharp decrease in ClO vibrational excitation, large translational energy release, and more anisotropic product angular distributions reflect the onset of a new OClO dissociation mechanism. This new mechanism, which opens in the higher energy region near the $A^2A_2 \leftarrow X^2B_1$ Franck–Condon maximum, involves direct dissociation of A^2A_2 levels over a large potential energy barrier.

ACKNOWLEDGMENTS

H.F.D. acknowledges valuable discussions with K. A. Peterson, H.-J. Werner, S. A. Reid, and A. Stolow. Some of the equipment used in this work was provided by the Office of Naval Research under Contract No. N00014-89-J-1297. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76F00098.

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