Femtosecond real-time probing of reactions. XI. The elementary OCIO fragmentation

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Femtosecond reaction dynamics of OCIO in a supersonic molecular beam are reported. The system is excited to the $A^2A_2$ state with a femtosecond pulse, covering a range of excitation in the symmetric stretch between $v_1 = 17$ to $v_1 = 11$ (308–352 nm). A time-delayed femtosecond probe pulse ionizes the OCIO, and OCIO$^+$ is detected. This ion has not been observed in previous experiments because of its ultrafast fragmentation. Transients are reported for the mass of the parent OCIO as well as the mass of the ClO. Apparent biexponential decays are observed and related to the fragmentation dynamics:

$$\text{OCIO} + h\nu \rightarrow (\text{OCIO})^+ \rightarrow \text{ClO} + \text{O}$$

Clusters of OCIO with water ($\text{OCIO}_n \cdot (\text{H}_2\text{O})_m$) with $n$ from 1 to 3 and $m$ from 0 to 3 are also observed. The dynamics of the fragmentation reveal the nuclear motions and the electronic coupling between surfaces. The time scale for bond breakage is in the range of 300–500 fs, depending on $v_1$; surface crossing to form new intermediates is a pathway for the two channels of fragmentation: ClO + O (primary) and Cl + O$_2$ (minor). Comparisons with results of ab initio calculations are made.

I. INTRODUCTION

The gas phase photodissociation mechanisms of OCIO in the near-UV region have stimulated copious experimental and theoretical studies (for recent references, see Refs. 1–13) due in part to its possible role in the depletion of ozone in the Antarctic stratosphere. The absorption spectrum of OCIO ($A^2A_2 \rightarrow X^2B_1$) spans from 475 to 273 nm (Refs. 15 and 16) (Fig. 1). At all absorption wavelengths, the major dissociation channel is found to be

$$\text{OCIO}(A^2A_2) \rightarrow \text{ClO}(X^2\Pi, \nu''') + \text{O}(3P),$$  \hspace{1cm} (1)

whereas a minor channel is

$$\text{OCIO}(A^2A_2) \rightarrow \text{Cl}(2P) + \text{O}_2(3\Sigma^-, 1\Delta_0, 1\Sigma^+).$$  \hspace{1cm} (2)

Since the O atom formed in reaction (1) could react with O$_2$ molecules in the atmosphere to produce O$_3$, this dissociation pathway would lead to a null cycle in stratospheric ozone depletion. Reaction (2), however, represents a mechanism for halogen-catalyzed conversion of O$_3$ to O$_2$. To understand the photodissociation mechanism of OCIO, different experimental techniques have been applied.

In describing the elementary nuclear motions of OCIO fragmentation, three coordinates must be considered—the symmetric stretch $v_1$, the bend $v_2$, and the asymmetric stretch $v_3$ (see Table I). Generally, for a given bend configuration, a wave packet on a single potential energy surface (PES) will evolve along the reaction coordinate from the bound symmetric stretch region of the PES (Fig. 2). Since the pump is not energetically broad enough to span levels of $v_1$, a localized wave packet is not created along the symmetric stretch coordinate. If a wave packet could be generated, the problem becomes analogous to the case of HgI$_2$, where coherent nuclear motion (Fig. 3) to yield HgI$^+$ was observed and studied. For OCIO, the problem is more complicated, however, due to the fact that several nearby potentials may be involved.

In this paper, in the series, we report studies of the ultrafast dynamics of OCIO elementary fragmentation using the techniques of femtosecond transition-state spectroscopy (for reviews, see Refs. 20 and 21). Of particular relevance here is the use of multiphoton ionization and mass spectrometry, which makes it possible to observe the parent ion of OCIO (i.e., OCIO$^+$) hitherto undetected by previous nanosecond experiments. We follow the initial nuclear motion and measure the real-time dissociation to different fragments. In the range of $v_1 = 11–17$, bond breakage times are typically 300–500 fs, while the initial decay ranges from 30 to 120 fs. We relate these observations to the nature of the dynamics and to recent ab initio calculations of the PESs. We also report results on the detection of one of the fragments (ClO) and preliminary studies of OCIO when selectively solvated with water.

The outline of the paper is as follows: In Sec. II, a brief description of the experiment is provided, followed by results and data analysis in Sec. III. The discussion presented in Sec. IV includes previous spectroscopic and beam work on OCIO as well as our contribution relating the femtosecond dynamics and mechanism of dissociation. Concluding remarks are given in Sec. V.

II. EXPERIMENT

The femtosecond laser apparatus has been described in detail previously and is discussed only briefly here. Fem-
tosecond pulses were generated from a colliding pulse mode-locked (CPM) ring dye laser and amplified by a Nd:YAG-pumped pulsed dye amplifier (PDA). The recompressed output pulses had an (unattenuated) energy of 0.2–0.3 mJ at a repetition rate of 20 Hz. The pump wavelengths in the range from 308 to 312 nm were generated by frequency doubling a part of the PDA output in a 0.2 mm thick KDP crystal; for these wavelengths, the CPM was tuned by proper adjustment of the saturable absorber concentration. In order to obtain the wavelength range from 312 to 352 nm, we focused part of the PDA output on a D₂O cell to produce a white light continuum. With 10 nm bandwidth interference filters, we selected the desired wavelengths from 624 to 704 nm; this light was further amplified in a longitudinally pumped dye cell before being doubled in a KDP crystal. For the multiphoton ionization (MPI) probe, we used the remaining output of the PDA at 620 nm.

The pump and probe beams, with proper attenuation and parallel or perpendicular polarization, were delayed in time relative to one another in a Michelson interferometer and were then recompressed collinearly and focused onto the OClO molecular beam. Before entering the molecular beam, we routinely recorded autocorrelations of the probe (∼80 fs sech²) and cross correlations between pump and probe (∼190 fs).

The supersonic molecular beam consisted of a pulsed nozzle with an orifice diameter of 0.3 mm. MPI experiments on the skimmed molecular beam were carried out in a differentially pumped ionization chamber about 12 cm downstream from the nozzle. The time-of-flight (TOF) detector had a field-free drift tube with a mass resolution of ∼1:150. The molecular beam, the lasers, and the TOF detection axes were mutually perpendicular. A sketch of the experimental arrangement is shown in Fig. 4.

OClO was produced in situ by flowing a 3.5% Cl₂/He mixture through a U tube packed with glass beads and

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**TABLE I. OCIO in C₂ geometry.**

<table>
<thead>
<tr>
<th>Frequency (\bar{v} (\text{cm}^{-1}))</th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
<th>(T_e (\text{eV}))</th>
<th>Reference</th>
</tr>
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<tbody>
<tr>
<td>(X^2{B_1})</td>
<td>963.5</td>
<td>451.7</td>
<td>1123.0</td>
<td>a</td>
<td></td>
</tr>
<tr>
<td>(2{B_2})</td>
<td>815.0</td>
<td>319.5</td>
<td>520</td>
<td>1.98</td>
<td>b</td>
</tr>
<tr>
<td>(2{A_1})</td>
<td>696.5</td>
<td>311.3</td>
<td>1474</td>
<td>2.04</td>
<td>b</td>
</tr>
<tr>
<td>(A^2{A_2})</td>
<td>713.2</td>
<td>278.1</td>
<td>401.5</td>
<td>2.68</td>
<td>c</td>
</tr>
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</table>

Symmetry of normal vibrations

<table>
<thead>
<tr>
<th>Normal vibration</th>
<th>(\nu_1)</th>
<th>(\nu_2)</th>
<th>(\nu_3)</th>
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<tbody>
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<td>Stretching ((\nu_1))</td>
<td>(a_1)</td>
<td>(a_1)</td>
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<tr>
<td>Bending ((\nu_2))</td>
<td>(a_1)</td>
<td>(a_1)</td>
<td>(a_1)</td>
</tr>
<tr>
<td>Asymmetric stretching ((\nu_3))</td>
<td>(b_2)</td>
<td>(b_2)</td>
<td>(b_2)</td>
</tr>
</tbody>
</table>

Electric dipole selection rules

- \(A^2{A_2} \rightarrow X^2{B_1}\) Parallel polarized
- \(2{A_1} \rightarrow X^2{B_1}\) Perpendicular polarized
- \(2{B_2} \rightarrow X^2{B_1}\) Forbidden

Allowed pairs of electronic states for vibronic coupling

- \(A^1 \rightarrow B_1\)
- \(A^1 \rightarrow B_2\)

* Taken from Ref. 60.
* Taken from Ref. 12.
* Vibrational constants were derived from Ref. 9. \(T_e\) was derived from Refs. 12 and 60.
* For rotations, see Ref. 62.
NaClO₂, following the procedure of Derby and Hutchison. In order to be below the detonation limit of OCIO, a constant total backing pressure of 1.5 atm was maintained for the expansion of OCIO. In concentrations in excess of 10% of atmospheric pressure, OCIO is easily detonated by sources of initiation such as sunlight, heat, or electric discharge.

III. RESULTS AND ANALYSIS

In Fig. 5, a TOF spectrum is shown for an excitation wavelength centered at 329 nm. This corresponds to the absorption peak 14 in Fig. 1, which is labeled spectroscopically as the (14 0 0) band. The probe laser (620 nm) was set at a time delay of 170 fs. A prominent feature in this resonance-enhanced multiphoton ionization (REMPI) TOF spectrum is the two OCIO isotopes. As mentioned above, OCIO⁺ ions have not been observed previously in nanosecond-laser REMPI experiments. The products in this spectrum are the two ClO isotopes. Sufficient cooling of our sample is obtained, as evident by the onset of the cluster formation. We also observe (OCIO)ₙ clusters with n = 1–3 and (OCIO)ₙ (H₂O)ₘ clusters with n, m = 1–3. No additional water was used in the heterogeneous OCIO–water cluster formation; the inherent moisture of the NaClO₂ provided enough water vapor pressure for clustering. All cluster mass channels are split due to the two Cl isotopes. The (H₂O)₃ cluster, prominent in the electron impact mass spectrum of Vaida et al., is not seen in this femtosecond pump–probe REMPI spectrum under the above conditions.

The femtosecond experiments on the mass-selected parent OCIO or fragments involve the following scheme of energy and mode excitations (Fig. 6): The initial excitation is from the (0 0 0) state (with relatively low hot-band excitation) of the X²B₁ ground state of OCIO to the A²A₂ state (the region between 3.54 eV). In the absorption spectra of Fig. 1, this excitation corresponds to bands 11 (351.3 nm) to 17 (311.5 nm). This transition is parallel...
FIG. 5. The TOF spectrum taken in a femtosecond pump-probe arrangement. Note that the prominent masses are the OCIO parent and the ClO product.

polarized; the perpendicular polarized transition into the \( ^1A_1 \) state, in principle allowed, has not been observed experimentally.\(^{13}\) The transition to the \( ^2B_2 \) state is dipole forbidden. In the energy range 7–8 eV (two pump photon excitation), only one-photon absorption spectra are reported,\(^{29,30}\) with very short progressions.\(^{30}\) As discussed below, two-photon excitations are minimized.

It takes four probe photons at 620 nm to ionize the system. A continuous increase of the one-photon absorption cross section from 6 up to 25 eV was measured by Flesch et al.,\(^{29}\) indicating that the probe laser ionization involves a REMPI process (vib in infra). The ionization potential of OCIO is 10.33 ± 0.02 eV.\(^{29}\) As shown in Fig 6, at least one additional probe photon (making a total of at least five probe photons) is required to reach the ionic fragmentation channel. The threshold for ClO\(^+\)(\( ^3\Sigma^- \)) + O(\( ^3P \)) is measured to be 13.45 ± 0.04 eV.\(^ {29}\) The \( D_0 \) value for the neutral ClO\(^{(2\Pi)}\) + O(\( ^3P \)) asymptote is given to be 55.2 ± 2 kcal/mol,\(^ {31}\) corresponding to ~2.4 eV. Taking into account the fact that the ClO fragments are vibrationally excited to the \( v'' = 3-6 \) range\(^7\) and knowing the vibrational frequency of ClO in its ground state (~0.1 eV),\(^{32}\) our total available energy with respect to ground state fragmentation is ~1 eV. Energetically, the next higher fragmentation channel leading to ClO\(^{(2\Pi)}\) + O(\( ^1D \)) would require a threshold energy of ~4.5 eV. Hence, the fragmentation channels leading to electronically excited ClO or excited O may be excluded from further consideration.

Typical femtosecond transients taken on \( ^{35}\)ClO and \( ^{37}\)ClO are shown in Figs. 7 and 8. The transients were taken at a pump wavelength of 329 nm at band 14 in Fig. 1. First we consider the \( ^{35}\)ClO transient in Fig. 7. From...
the insert, plotted on a logarithmic scale, it is evident that the transient shows a biexponential decay. The cross correlation, also shown in the insert, is symmetric and different from the initial decay. The time constants, derived from a molecular response function of the type

$$M(t) = Ae^{-t/\tau_1} + Be^{-t/\tau_2} \quad (A + B = 1),$$

are $\tau_1 \sim 50$ fs, $\tau_2 \sim 400$ fs, and $A \sim 0.89$ for this transient. These results depend on the initial excitation energy and are not consistent with a simple sum of a decay and an off-resonance ionization signal (vide infra). The values for $\tau_2$ are much larger than our response function; in order to obtain accurate values of $\tau_1$, we convoluted the transient form of Eq. (3) with the measured cross correlation taken carefully before and after the experiments (Fig. 7).

Care was taken in considering several control experiments. First, according to the energetics of this system (Fig. 6), the process requires one pump photon and four probe photons. The laser intensities were therefore adjusted such that the pump laser alone did not produce an appreciable MPI signal. Typical values were a maximum of 10% MPI signal from the pump laser alone relative to the MPI level of the stronger probe laser. The maximum signal enhancement was then typically two to three times greater than the time-independent background consisting of the sum of pump and probe MPI levels.

Second, while the pump (alone without the probe) MPI background signal vs intensity showed an approximate quadratic power dependence, the total signal due to pump plus probe vs pump laser intensity showed an approximate linear power dependence. Probe laser intensity studies showed a similar behavior.

Third, the ratio $A/B$ of the amplitudes of the two time constants [Eq. (3)] did not change by attenuating the pump laser, as would be expected if one of the time constants were due to a two-photon or off-resonance excitation. It is known from similar work that the pump laser intensity does not affect the time constants in a femtosecond MPI process (where one-photon excitation dynamics and two-photon excitation dynamics contribute to the observed transient ionization signal), yet the ratio of these contributions is very sensitive to intensity. A further indication of the approximate linearity of the total signal in these experiments is that the rise of the transients could be fitted nicely to the cross correlation (measured in front of the molecular beam apparatus).

Fourth, parallel or perpendicular polarization of our lasers had no significant influence on our transients, neither on the observed time constants nor on the $A/B$ ratio. Most of the experiments were performed with perpendicular polarization.

Tuning the laser from $v_1$ band 17 to band 11 resulted in an increase of $\tau_2$ from about 30 to about 120 fs. The second time component also increased from about 300 to $\sim 300$ fs. This increase in the time constants with respect to lower excitation energies is accompanied by a decrease of the $A/B$ ratio of the two time components; the fast component was always found to be the dominant contribution. These trends are summarized in Fig. 9.

From the high-resolution work of Vaida et al., it is known, at least for the low excitation regime, that to the blue side of every pure symmetric stretch excitation, a ($v_1 \ 0 \ 2$) band is observed (in addition to other combination bands). The rotational line broadening analysis suggests significant broadening of the ($v_1 \ 0 \ 2$) band compared to the symmetric stretch alone ($v_1 \ 0 \ 0$). Tuning the central wavelength of our femtosecond-pump laser up to 4 nm to the blue side of the (14 0 0) band did not yield significant changes in the two time constants. Thus, the "mode selectivity" seen in the low excitation regime seems to be blurred in the high-excitation region of the spectrum, where mode-specific structure also appears to "wash out" in the low-resolution spectrum (Fig. 1). Note that this small tuning is comparable to the full width at half-maximum (FWHM) ($\sim 3.5-4$ nm) of the pulse. If the transient were composed of a superposition of two components (decay and off-resonant ionization), we would have expected changes in the $A/B$ ratio of the fast and slow components associated with tuning the central wavelength of the pump from a maximum in the low-resolution spectrum to as much as 4 nm away.

In addition to the above results on the parent molecule, we also studied the transients of the observed mass fragments. The ClO transient in Fig. 8 resembles the OClO transient, also shown in this figure, but there are two differences. First, the rise of the ClO transient is shifted with

![FIG. 9. Pump wavelength dependence of the two time constants and the $A/B$ ratio. The peak numbers correspond to the numbers given in Fig. 1 for the vibrational stretch quantum number. The points where error bars are shown represent data sets that include enough measurements to give a meaningful standard deviation.](image-url)
respect to the rise of the OCIO transient by 20-40 fs. This shift is real, as the ClO transients were recorded with the same experimental conditions as the OCIO transients, by only changing the detection electronics (gate of a boxcar) from the mass of the OCIO to the mass of the ClO. The shift is displayed in the inset of Fig. 8. Second, the final value of ClO+ reaches an asymptote of 15% to 25% of the total signal, as seen in Fig. 8. On a time scale of up to 15 ps (the maximum pump-probe delay in these experiments), this final value remained constant.

Power dependence studies also showed an approximate linear dependence of the total signal with respect to pump and probe laser intensities. The fact that the ClO signal reaches a final value is consistent with the expectation that the neutral fragmentation of OCIO leads to ClO+O after the pump-pulse excitation. As the I.P. of ClO is 11.01 ±0.01 ev,34 it takes six photons of our probe laser to ionize this species. This nonzero ClO signal at all excitation wavelengths (including 308 nm, where previous femtosecond experiments were performed) is formed on the femtosecond time scale and remains for long times.

For the short-time behavior, the OCIO and ClO transients match in shape, but, of course, with the time shift. This suggests that they have the same origin; they are directly related to the fragmentation dynamics of the OCIO. Note that only one additional probe photon is needed to reach the ionization fragmentation channel from the initial OCIO ground state (Fig. 6). Typical time scales in the ionized ground state are ~35 fs for the symmetric stretch and ~70 fs for the bending motion.29 These times correspond to the observed shift of about 20-40 fs of the ClO+ transient with respect to the OCIO+ transient. We therefore suggest that the time shift is due to the propagation of a wave packet in the OCIO+ ground state from the region initially excited by four probe photons into a region where the Franck-Condon (FC) factors are more favorable for the ClO+ + O fragmentation. Absorption of a fifth probe photon would then lead to such fragmentation. The transient of the ClO+ thus reflects both the neutral product formation and then ionization (long-time constant level) and the parent OCIO ionization and subsequent ion fragmentation with decay (short-time behavior).

IV. DISCUSSION

A. Spectroscopic and beam studies

In the high-resolution absorption spectra of OCIO by McDonald and Innes3 and Michielsen et al.,5 the rotational structure of the symmetric-stretch progression was investigated for \( v_1 = 1 - 5 \). It was found that the rate of "predissociation" (\textit{vide infra}) depends on the spin state prepared. The rate is greater for the \( F_1 \) (\( J = N - 1/2 \)) state than for the \( F_2 \) (\( J = N - 1/2 \)) state and is independent of the rotational state of the initially excited molecule. In addition, it was found that for \( v_1 < 3 \), the rate of predissociation from the states (\( v_1 0 0 \)) is independent of \( v_1 \), but for \( v_1 > 3 \), the rate increases with \( v_1 \). For example, the lifetime of the \( F_1 \) component in the (\( 0 0 0 \)) state is given to be 67±14 ps, while for the (\( 5 0 0 \)) band, 28±1 ps is reported.2 It is further noted that the bending mode shows faster predissociation rates at comparable energies. According to the two-dimensional cuts through the "\textit{ab initio}" PES along the symmetric stretch, bend, and asymmetric stretch coordinates calculated by Peterson and Werner17 (Fig. 2), the system is bound along the first two and unbound along the asymmetric stretch.

Direct vibronic coupling of the \( 2A_2 \) state to the close lying \( 2B_2 \) and \( 2A_1 \) states is forbidden for this triatomic in \( C_{2v} \) symmetry, while allowed to the \( 2B_1 \) ground state.35 McDonald and Innes3 have argued that it is unlikely that the \( 2B_1 \) ground state couples with the prepared \( A \) \( 2A_2 \) state, as the observed vibrational and spin dependencies of the rotational linewidths could not be reasonably explained by such coupling of the excited manifold. As the bending mode is promoting the predissociation and the \( 2B_1 \) state is strongly bent (Fig. 2), Michielsen et al.7 and McDonald and Innes3 concluded that the \( 2A_2 \) state mixes with the \( 2B_2 \) state by spin orbit coupling before proceeding to dissociation. Recent calculations by Peterson and Werner12 of the PES and a closer analysis of the possible excited-state interactions with respect to symmetric stretch, bend, and asymmetric stretch coordinates prefer the \( 2A_1 \) state as the state from which the predissociation proceeds.

Vaida and co-workers10 provided the analysis of rotational line broadening involving \( (v_1 0 0), \ (v_1 1 0), \) and \( (v_1 0 2) \) bands of OCIO, extending the range from \( v_1 = 4 - 10 \). The absorption spectrum was measured directly using jet-cooled Fourier transform ultraviolet spectroscopy.45 They observed an increase in \( \text{fitted} \) rotational linewidths, and thus a decrease in the corresponding lifetimes from about 20 ps at \( (5 0 0) \) to about 4 ps at \( (10 0 0) \) (see Fig. 3 in Ref. 10). In studying modes involving bending excitation, linewidths were found to be four to five times broader than for the symmetric stretch alone at the same energy. It was also found that combinations involving \( v_1 \) with \( 2v_3 \) broaden more rapidly than combinations of \( v_1 \) with \( v_2 \). The experimental observations were explained via interactions of the PES and a closer analysis of the possible excited-state interactions with respect to symmetric stretch, bend, and asymmetric stretch coordinates calculated by Peterson and Werner12 (Fig. 2). In the excitation region higher than \( v_1 = 10 \), it is reported that the linewidths appear to reach a limit and become fairly constant with lifetimes. A more detailed analysis of rotational linewidth broadening is not given in this energy region, as the individual rotational linewidths become too broad and thus only the rotational envelopes are discernible (Fig. 10). Estimates of the lifetimes, however, are given at 303 nm (\( v_1 \) between 18 and 19) to be ~1 ps, and for the \( v_1 = 4 \) level at 333 nm, linewidths of ~100 cm\(^{-1}\) (~50 fs) were reported with the note that these bands are disappearing into noise.14

Experiments involving nanosecond-laser REMPI techniques have also been reported: Vaida's group recorded spectra in the range from 335 to 370 nm which focused on the \( \text{ClO}^+ \) and \( \text{Cl}^+ \) channel,7 however, the parent OCIO\(^+\) was not seen.15 Ionization and fragmentation are two competing channels, and with nanosecond pulses, "channel switching," discussed by Schlag and Neussner36 and Taylor and Johnson,37 can lead to ionization of fragments and not...
of the parent neutral. Such behavior has previously been demonstrated in methyl iodide, where the CH$_3$I$^+$ and fragment I$^+$ were observed to vary in intensity depending on the delay time between the pump and MPI pulses. Another example comes from the work of Gerber's group on Na$_n$ cluster resonances. When, e.g., $n > 4$, the absorption spectra of the Na$_n$ clusters could not be measured directly by nanosecond-laser REMPI techniques due to the fast fragmentation processes of the excited intermediate states. However, femtosecond-laser REMPI techniques were successful in observing these resonances as well as determining the lifetimes of the intermediate states directly in the time domain via pump–probe experiments. The product analysis in Vaida's group's work indicated that for the O$^2P$ + ClO$^X$($^2$H) fragmentation, the Cl$^+$ molecules were released vibrationally excited ($v'' = 3-6$).

They also observed Cl$^+$ REMPI action spectra in the region 360–363 nm and attributed this observation to an isomerization of OCIO to ClO$_2$, which subsequently dissociates to Cl$+$O$_2$. The quantum yield for Cl formation was reported by Lawrence et al. to be less than $5 \times 10^{-4}$ between 359 and 368 nm, an upper limit as they did not actually observe Cl$+$O$_2$. A further REMPI experiment was reported by Bishenden et al., who used a tunable dye laser to excite OCIO in the wavelength range 355–370 nm and probed Cl via a (2+1) REMPI process near 235 nm. In contrast to the work of Lawrence et al., the quantum yield near 362 nm for the formation of Cl was given to be 0.15 $\pm$ 0.10. The REMPI spectrum of Bishenden et al. reproduces the OCIO absorption spectrum, suggesting that the Cl$^+$ signal does result from OCIO dissociation.

However, recent studies by Davis and Lee, who measured the Cl yield from 350 to 475 nm by photofragment translational energy spectroscopy, found that the total yield of Cl production is only important near 404 nm, where a maximum of 3.9$\%$ $\pm$ 0.8$\%$ is reached; the yield between 350 and 370 nm is below 0.2$\%$. In order to explain these discrepancies, Davis and Lee suggested that the high yield in Bishenden's REMPI spectrum is due to photodissociation (by the probe laser) of the ClO product followed by REMPI (2+1) detection of Cl atoms within the time duration of the nanosecond-probe laser used in the experiments. A further result of their work is that the yield of Cl$+$ from symmetric stretch or symmetric stretch plus bend excitation is $\sim$10 times greater than the yield from states at nearly the same energy with asymmetric stretch excitation. To explain this mode-specific behavior, it was proposed that the symmetric stretch and the bending modes favor coupling into the $^2B_2$ state whose equilibrium angle is near 90$^\circ$ (Fig. 2). On this state then, OCIO undergoes a concerted decomposition from a transition state geometry close to $C_{2v}$, rather than an isomerization process to form ClOO followed by a unimolecular dissociation. This is consistent with the theoretical analysis of Gole, who suggested that vibronic coupling to nearby states plays an important role in the Cl$+$O$_2$ channel.

Glownia et al. have reported on the absorption, in a static gas cell, of OCIO in femtosecond pump–probe experiments. OCIO was excited by a pump pulse at 308 nm, while the ClO product was monitored by the absorption of a continuum probe pulse in the wavelength region between 268 and 278 nm. No ClO was detected on a time scale of up to 1 ns. Using a 308 nm nanosecond excimer laser as a pump and the femtosecond continuum laser as a probe, however, ClO absorption built up after several hundred nanoseconds. Vaida et al., who detected the formation of Cl$^+$ within the nanosecond laser pulse at 308 nm, attributed the unexpected (very long) observed time scale of Glownia et al. to the collisional relaxation of the vibrationally excited Cl$^+$. From the above discussion, the time scales for predissociation in the energy range up to $v_1$ = 10 are inferred from linewidth measurements. The yield of ozone-destroying Cl in this photodissociation process seems to be minor, especially in a wavelength regime below 370 nm. The corresponding predissociation mechanisms for this Cl$+$O$_2$ channel are interpreted in terms of various interactions of the initially excited $^2A_1$ state with the two lower-lying $^2A_1$ and $^2B_2$ states. In what follows, we consider the femtosecond dynamics in the high energy excitation regime of $v_1$ = 11–17. The observation of the femtosecond decay of the initially excited states gives direct measure of the dissociation. From the shape of the femtosecond transients and the energy dependence, we examine the mechanism and the dynamics of prompt OCIO dissociation to ClO+O vs the indirect dissociation, involving nearby potentials, in the ClO+O and Cl+O$_2$ channels.

B. Femtosecond dynamics and mechanism

The observed biexponential decay of OCIO over the entire range of $v_1$ studied indicates that the dynamics do not reflect a direct process only. There are a number of characteristics which assign the origin of the observed behavior. First, the decay constant of the fast component, which ranges from about 30 fs at $v_1$ = 17 to about 120 fs at $v_1$ = 11 is different from the two pulse cross correlation; as mentioned before, the cross correlation is symmetric, whereas the fast component is not. Second, the slow component of the decay, which ranges from about 300 fs at $v_1$ = 17 to about 500 fs at $v_1$ = 11, depends on the excitation energy. Third, the ratio of the fast to slow component, which does not change with intensity (pump or probe)
changes with \(v_1\), but not when the pump is tuned within a specific \(v_1\) band (~4 nm range). From these observations, we conclude that the fast component is not an "off-resonance" transient peak, consistent with the fact that the pump is tuned to the strong absorption of the \(v_1\) bands and not to an off-resonance absorption region. The fact that we did not see a change in the transient behavior over a given range of \(v_1\) indicates that there is no mode selectivity at these high energies and that homogeneous dynamics from an initial state are operative. For example, one may attribute the fast component to a level involving the asymmetric stretch \(\text{ClO} + \text{O}\) products channel and the slow component to the symmetric stretch level which ultimately produces \(\text{Cl} + \text{O}_2\). However, this assignment is inconsistent with the \(A/B\) ratio as the absorption of the \(v_1\) dominates, and also the yield for the \(\text{Cl} + \text{O}_2\) channel at 350–370 nm is less than 0.2%.\(^{11}\)

The simplest mechanism to emerge involves the decay of the \(v_1\) state on the \(^2A_2\) potential and the formation of intermediates of \(\text{OCIO}\) on the nearby PES(s). The reaction involves the following elementary steps:

\[
\begin{align*}
\text{OCIO}_{(v_1=2, A_2)} \rightarrow & \text{ClO} + \text{O} \\
\rightarrow (\text{OCIO})_{(v_1=1, A_2)} \rightarrow & \text{Cl} + \text{O}_2.
\end{align*}
\]

The total rate of the initial decay is determined by both \(a + b\) channels. Fundamentally, process \(a\) is the one described in Fig. 3. Excitation of the symmetric stretch is bound provided the system is along the line of the saddle (in a deterministic classical picture), but of course any motion (even zero-point motion) can take the system into the second dimension of the asymmetric stretch to yield \(\text{ClO} + \text{O}\). In an adiabatic picture (and on one surface), \(v_1\) excitation in the transition-state region leads to \(v''\) excitation in OCl with a net translational energy for the recoil of OCl and O. We can estimate the time scale for this process based on the energetics, assuming a simple exponential repulsive potential. Taking the steepness of the potential to be 0.7 bohr (0.37 Å) (extrapolated from the asymmetric stretch coordinate in Fig. 2), and knowing that the translational energy release is about 1 eV (the excess energy above the \(\text{OCIO} + \text{O}\) threshold minus the internal energy of \(\text{OCIO}\)), the time for bond breakage [at 5.5 bohr (see Fig. 2)] is approximately 40 fs.\(^{20,21,39}\) Naturally, at least 2D calculations are needed for accurate comparisons.

The total rate for producing the intermediate(s) \((\text{OCIO})_{(v_1=1, A_2)}\) in different vibrational levels \((v)\) of the lower-energy \((|l\rangle)\) PES(s) via channel \(b\) is determined by the effective coupling of the \(^2A_2\) state to the nearby \(^2B_2\), \(^2A_1\), or to the ground state \(^2B_1\). Quantum mechanically, one must consider the coupling of the \(|^{2A_2,v_1}\rangle\) level to the quasien-ergic levels of the intermediate which then couple to the translational continuum of the \(\text{ClO} + \text{O}\) or \(\text{Cl} + \text{O}_2\) channels. This type of coupling (see Fig. 11) can find analogies in the problems of intramolecular vibrational-energy redistribution (IVR) and nonradiative decay (for reviews, see Refs. 40 and 41). To compare with experimental rates, we adapt a simple kinetic model (biexponential decay) which captures the essence of the quantum treatment, keeping in mind that the fundamental limitation of the kinetic description is the absence of coherence.\(^{40,41}\) This type of two-step model has been invoked in describing similar biexponential behaviors associated with the dynamics of IVR in stilbene by MPI,\(^{22}\) IVR/predissociation of van der Waals complexes by fluorescence or MPI,\(^{24,62}\) and more recently for H-atom transfer.\(^{43}\) Biexponential decay has also been observed in relation to interelectronic state coupling.\(^{46}\)

In the case of \(\text{OCIO}\), the initial state \(|^{2A_2,v_1}\rangle\) \((\equiv |1\rangle)\) in Fig. 11 undergoes energy redistribution into the manifold of the lower-energy surfaces followed by the relatively slow overall decay of the "equilibrated" distribution to give products. Designating the decay constant of the initial non-stationary state by \(k_1\) and the equilibrated distribution by \(k_2\), one can obtain an expression for the population change with time. Ionization out of the \(|1\rangle\) state is described by an effective four-photon ionization cross section \(\sigma_1\), and by \(\sigma_2\) for ionization out of the \(|2\rangle\) manifold. Solving the corresponding rate equations leads to a molecular response function for the ion yield \(M(t)\) as a function of pump-probe delay time \(t\) of the form

\[
M(t) = 0, \quad \text{for } t < 0, \\
M(t) = (\sigma_1 - \sigma_2 K)e^{-k_1t} + \sigma_2 Ke^{-k_2t}, \quad \text{for } t \geq 0.
\]

In Eq. (5), the linear pump excitation is invoked and \(K\) is given by \(k_1/(k_1 - k_2)\). The expression for \(M(t)\) given here is related to \(M(t)\) in Eq. (3) by \(A = \sigma_1 - \sigma_2 K, B = \sigma_2 K, \tau_1 = 1/k_1, \tau_2 = 1/k_2; \) the ratio \(A/B\) is given by \((\sigma_1/\sigma_2)[(k_1 - k_2)/k_1] - 1.\) In Ref. 22, the explicit influence of a resonant intermediate for probing in this kind of model is investigated. It was found that only the ratio of the two rates is affected, not the rates themselves. For this reason, we describe our four-photon probe process by an effective ionization cross section \((\sigma_1 + \sigma_2)\) (vide supra). Note that we have neglected reversibility of \(|2\rangle\) to \(|1\rangle\) based on the relative density of states. However,
should be on the order of $10\sigma_2$ for typical time constant and amplitude values (Fig. 9), otherwise the response function would not have an instantaneous rise. REMPI probing from two different electronic structures could explain different ionization cross sections simply by different selection rules or ionization potentials for the four probe photons involved in the ionization process.

The nature of the $(OCIO)_2^{+}$ intermediate depends on the potential. On the ground state $^{2}B_1$, the intermediate is a vibrationally hot ground state molecule with energies of $\sim 1$ eV above dissociation (Fig. 2) to ClO+O. In $C_{4v}$, Herzberg–Teller vibronic coupling is allowed between $^{2}A_2$ and $^{2}B_1$ as the direct product contains the $b_1$ irreducible representation of the asymmetric stretch vibration. In Ref. 3, this route was considered less likely at lower energies because of the selectivity in line broadening with respect to the spin state prepared and the “large” density of states. At higher energies, the situation is different, particularly that the number of states is increased significantly. We can estimate the time scale for the decay of the “equilibrated” ($|2\rangle_{\nu}$) distribution, described by $k_2$, by calculating the rates based on microcanonical transition-state theories. This is similar to the treatment given in Ref. 48 for the dissociation of NCNO. However, since the energy above dissociation is large ($\sim 1$ eV), we expect the transition state to be more of a tight type. Accordingly, we adopted the simple Rice–Ramsperger–Kassel–Marcus (RRKM) expression

$$k(E) = \frac{N(E)}{E} \rho(E)$$

(6)

for an order-of-magnitude estimate. In Eq. (6), $N(E)$ is the number of states in the transition state at energy $E$, excluding the reaction coordinate. $E_0$ denotes the reaction threshold, while $\rho(E)$ is the density of states of the reactant. The estimate was made by taking the vibrational frequencies from Peterson and Werner (see also Table I) for the three electronic states under consideration (ignoring anharmonicities). $E_0$ was chosen to be $D_0$ for the $X^{2}B_1$ ground state. Taking the degeneracy of the problem into account (both bonds are equivalent), we multiplied the calculated rates by a factor of 2. Expressed in lifetimes, we obtain the following results by this estimate: the $X^{2}B_1$ state shows increasing decay times from 90 to 130 fs in the wavelength range from 310 to 350 nm. Similar estimates were made for the other states. Decay of the $^{2}B_2$ state results in a constant fragmentation time of about 30 fs in this energy range. The $^{2}A_2$ state shows an increase in the decay times from 30 to 50 fs.

The experimental observation of an increase of the slow time constant from about 300 fs at 310 nm excitation to about 500 fs at 350 nm excitation is in agreement with RRKM trends, which shows an increase of the decay time with decreasing excitation energy. The fact that tuning the pump laser in small energy ranges (up to 4 nm) did not affect the decay times is consistent with the interpretation that the biexponential decay is due to energy redistribution followed by a decay of a distribution of levels of the intermediate(s) formed. As mentioned above, the calculation of $k(E)$ is intended to serve as an order-of-magnitude estimate and more accurate calculations, similar to those done on NCNO (Ref. 50), are underway. We also plan to compare with calculations made for analysis of the recent sub-picosecond study of NO$_2$ dissociation by the Wittig group.

In the preliminary study of the OCIO–water clusters, we have observed the fast component, but the signal-to-noise ratio was not (yet) good enough to obtain an accurate ratio of $A/B$. It is consistent to see a fast (or faster) component as we expect the cluster modes to help the energy redistribution.

The Cl+O$_2$ products channel also involves the coupling of two potentials. The transition from the ground state $^{2}B_1$ to the $^{2}A_2$ state results in the promotion of an electron into an orbital ($b_1$) which is Cl–O antibonding, but O–O bonding. The bond angle decreases accordingly from $117^\circ$ to $107^\circ$ and the Cl–O bond length increases from 1.47 to 1.62 Å. Even though the bond angle decreases, the increase in bond length requires very large amplitude motion for concerted Cl$_2$+Cl to occur. However, if the intermediate (OCIO)$^2$ has some population on the $^{2}B_2$ surface, then this intermediate will be produced with a compressed angle of $\sim 90^\circ$ (see Fig. 2); the electronic coupling between $^{2}A_2$ and $^{2}B_2$ provides a sensible route for having the two oxygens closer to each other on the $^{2}B_2$ surface. (The $^{2}A_1$ state may be involved indirectly.) To break the bond, the molecule in the transition-state region of the $^{2}B_2$ surface, which is rather strained, will concertedly release a large amount of kinetic energy, consistent with the beam experiments of Davis and Lee.

However, the rate of crossing into this transition state will depend, at a given energy, on the vibrational energy redistribution on the $^{2}B_2$ surface and, in particular, on the bend time scale. If we relate (in part) our long decay (hundreds of femtoseconds depending on $\nu_1$) to such a crossing, then only a few bend motions (see Table I) are required, since the period is about 100 fs. Once the system gets into the transition-state region, within a vibrational period Cl and O$_2$ separate yielding the large release of kinetic energy. Because of this barrier crossing and downhill kinematic, the translational energy distribution will not reflect the rate. The initial state absorption linewidth measurement, even if homogeneous, as discussed below, will not give the dynamics of this or the $^{2}B_1$ intermediate.

The coupling of the $^{2}A_2$ to the $^{2}B_2$ potential is by spin–orbit coupling and is not allowed in $C_{2v}$ by a Herzberg–Teller mechanism ($A_2 \otimes B_1 = b_1$). Also in $C_{2v}$ this coupling is not allowed. Thus, the interplay between the spin–orbit coupling to $^{2}B_2$ and the vibronic coupling to $^{2}B_1$ determines the nature of the intermediate, and at higher energies, where the $^{2}B_1$ density of states is increasing, vibronic coupling may become the dominant interaction. This brings to focus two points. First, the yield for Cl+O$_2$ [promoted by the bending mode (see Ref. 11 and the previous section)] as this excitation represents a promoting mode to the ClO+O channel via vibronic coupling. Additionally, the trapping of ClO$_2$ in
matrices by Arkell et al.,52 which suggested the isomerization of OCIO to ClO2, may be the result of an interesting change in dynamical time scale. With energy dissipation to phonons, the intermediate (e.g., \(2B_2\)) could cool down and the rate of crossing the transition state would become slow enough to compete with isomerization into ClO2.

To be complete, we must address the linewidth problem. At the energies studied here, Vaida's group reported the high resolution spectrum (Fig. 10). From the fit of a rotational band contour, they inferred a width of \(\approx 4\) ps for \(v_1 = 10\) and indicated that these widths “saturate” giving a value of \(\approx 1\) ps at 303 nm (\(v_1\) between 18 and 19). Several points must be considered. The mechanism discussed above reflects “overlapping resonances” because of the coupling with lower energy potentials. This results in a background and it is impossible to consider the system as homogeneously broadened in the sense of a two-level problem with \(\Delta V_{\text{width},\text{cm}^{-1}} = 1/(2\pi\tau_r)\) (for a Lorentzian line shape). Second, there is a finite convolution due to the inhomogeneous rotational distributions of both states. For \(v_1 = 11\), as an example, the two components of OCIO decay are \(\tau_1 = 120\) fs and \(\tau_2 = 500\) fs. We therefore expect a broad component of \(44\) cm\(^{-1}\) and narrower resonances of \(11\) cm\(^{-1}\) within this envelope. The high-resolution linewidth has a large apparent width (\(\approx 40\) cm\(^{-1}\)) which is comparable to the \(44\) cm\(^{-1}\) broadening, but clearly does not give the separate true dynamics of the initial state and the intermediates (bond breakage).

An envelope of \(44\) cm\(^{-1}\) must be less than the \(\Delta V_{\text{t}}\) separation (\(\approx 700\) cm\(^{-1}\)) in order for the \(v_1\) progression to be observed and “predissociation” to be identified. Indeed, this is experimentally true, and brings another important point—the excitation in the \(v_1\) manifold is in the transition-state region of the \(2B_2\) potential. The \(v_1\) “sharp” progression is therefore the (transverse) vibrational structure of the transition state,53 and to be observed, the lifetime for motion along the asymmetric stretch must be longer than the symmetric stretch vibrational period. In the example given above, the spacing between the \(v_1\) transitions is \(\approx 16\) times greater than the width of an individual \(v_1\), indicating that the lifetime is longer than the symmetric vibrational period by a factor of \(\approx 3\) (note that even if the lifetime and the vibrational period are the same, the ratio of the separation to linewidth is \(\approx 6\) because of the \(2\pi\) factor on going from lifetime to width). If the potential along the symmetric stretch is anharmonic, then the period will be even longer than that determined by the \(v_1 = 1\) frequency. When there is separation of the symmetric stretch transitions, one speaks loosely of “predissociation,” but it should be noted that this is not vibrational predissociation in its strict sense, where vibrational energy transfer is part of the dissociation dynamics [as, e.g., in the dissociation of van der Waals complexes \((A_2-X)\)]. The analogy made here with excitations to the transition-state region is similar to the case of \(\text{H}_2\text{S}_2\) discussed above17-19 and to the photodetachment experiments of Neumark et al.54 where direct absorption has been made. Butler has made this analogy between absorption and “resonance” dynamics recently.55 For OCIO, the initial transition-state region excitation and coupling with nearby surfaces are the two key dynamical features for the elementary fragmentation to OCICl + O and Cl + O2.

V. SUMMARY AND CONCLUSIONS

This contribution presents femtosecond real-time studies of OCIO elementary fragmentation in a supersonic molecular beam. Mass-spectrometry detection has been used to identify the reactants, products, and some selective clusters of OCIO with water. These dissociation products OCIO, O, and Cl (and the isomer ClO2) played an important role to the first millisecond flash photolysis experiments56,57 and to the ozone depletion problem.58 Here, the wavelength range from 308 to 352 nm was covered, corresponding to symmetric stretch excitation of \(v_1 = 17-11\). The parent ion OCIO+ is observed here with femtosecond pulses, making it possible to monitor the initial dynamics of OCIO. This ion was not detected in nanosecond-laser REMPI experiments performed in this excitation energy range due to the efficient ultrafast photochemistry.

The observed decay shows a biexponential behavior; both time constants decrease with increasing excitation energy. The form of the transients and their change with energy reflects the reaction intermediates, and our analysis considers the nearby potentials \((2B_2,2A_1)\) and the ground state \((1B_1)\) as the source of interaction. In addition to the direct fragmentation to ClO+O, the dissociation proceeds through the intermediates to give the primary products ClO+O on the ground state and/or the minor products Cl+O2 on the \(2B_2\) state. The change in the relative yield, the kinetic energy release, and the increase or decrease in the rates with selective vibrational modes (e.g., bending or asymmetric vibrations) are consistent with our picture. Furthermore, the change in bonding upon excitation, the nature of the transition-state on both surfaces, and the calculated rates of the reaction support the conclusion. Some comments on the relevance of linewidth measurements are made, emphasizing the insensitivity of the width to the dynamics of the intermediates and the inhomogeneity due to overlapping resonances and rotational convolutions.

The observed ClO transient reflects two different contributions—ionic fragmentation, showing a similar (but time-shifted) transient as the parent OCIO at short delay times, and neutral fragmentation leading to a final nonzero value of ClO\(^+\) at longer delay times. It was shown that the neutral fragmentation of OCIO excited by a femtosecond laser pulse at 308 nm leads to ClO formation on a time scale of a couple of hundred femtoseconds. Previous work reported no ClO appearance up to several hundred nanoseconds.

The preliminary studies of OCIO clusters with water \((\text{OCIO})_n(\text{H}_2\text{O})_m\) with \(n\) ranging from 1 to 3 and \(m\) from 0 to 3 opens up the possibility to study the heterogeneous photochemistry of these species in the time domain. We plan to extend the femtosecond dynamics studies reported here to these clusters and also to lower energies in isolated OCIO and the related systems of ClOCl and ClONO2.59
Theoretical wave packet 2D studies, similar to those made on 1HgI, are part of these efforts.

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44 A. W. Richardson, R. W. Redding, and J. C. D. Brand, J. Mol. Spectrosc. 29, 93 (1969); see also Ref. 61.
46 The rotational constants of OCIO have been determined in Ref. 60 and references therein. Relevant to this work, from the available data, we calculate the rotational dephasing (Ref. 63) based on the values of the constants $A = 1.056$ cm$^-1$, $B = 0.309$ cm$^-1$, and $C = 0.281$ cm$^-1$. At a rotational temperature of $T = 50$ K, we calculate a dephasing time of $1$ ps, longer than the observed time scales of the decay. This indicates the igniscence of the rotational contribution to the initial decay. The lack of large polarization anisotropy on the signal is most likely due to the four-photon MIPO mode of probing.