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CHEMICAL SCIENCES DIVISION

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# Dynamics and Mode Specificity in OClO Photodissociation

H.F. Davis and Y.T. Lee

March 1992

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(Submitted as a Letter to J. Phys. Chem.)

# DYNAMICS AND MODE SPECIFICITY IN OClO PHOTODISSOCIATION

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March 1992

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## Abstract

The photodissociation of OClO in a molecular beam was studied using photofragment translational energy spectroscopy at wavelengths between 350 and 475nm. Although the dominant products are $ClO(^2\Pi) + O(^3P)$, we observe formation of $Cl(^2P) + O_2(^3\Sigma^-_g)$, and find strong evidence for $Cl(^2P) + O_2(^1\Delta_g)$. The total yield reaches a maximum of $3.9\pm0.8\%$ near 404nm and decreases to $<0.2\%$ below 370nm. The branching ratios display mode specificity: the yield of $Cl + O_2$ from OClO with symmetric stretching excitation or symmetric stretching + symmetric bending is ~10 times greater than from states at nearly the same energy with asymmetric stretching excitation. The $Cl + O_2$ results from concerted unimolecular decomposition with release of up to ~68 kcal/mol in relative translational energy.

## Introduction

Although the $OClO(A^2A_2 \leftarrow X^2B_1)$ absorption spectrum in the near ultraviolet is now reasonably well understood,[1-3] the photodissociation dynamics remain uncertain.[3-8] At all absorption wavelengths, the dominant fate of excited state OClO is thought to be dissociation to $ClO(^2\Pi) + O(^3P)$.[2-4] However, a second decomposition pathway may be important:

$$OClO\ (X^2B_1) \xrightarrow{h\nu} OClO\ (A^2A_2) \rightarrow Cl(^2P) + O_2\ (^3\Sigma^-_g, ^1\Delta_g, ^1\Sigma^+_g) \qquad (1)$$

Whereas the ClO + O channel leads to a null cycle in the balance of atmospheric ozone, a substantial quantum yield for $Cl + O_2$ upon photolysis of OClO in the near ultraviolet would represent an additional mechanism for halogen catalyzed conversion of $O_3$ to $O_2$.[4-7] Although it is now apparent that heterogeneous processes contribute to the depletion of ozone,[9] a clear understanding of the photochemistry of atmospheric molecules under collision free conditions is required before addressing other complicating factors, such as perturbations by solvent molecules or adsorption on ice crystals.

Vaida and coworkers[4] studied the photodissociation of OClO in a molecular beam and confirmed that the dominant process was formation of $O(^3P) + ClO(^2\Pi)$. They also observed an additional feature in the Cl atom REMPI spectrum at 362nm that they attributed to isomerization of OClO to ClOO, followed by dissociation to $Cl + O_2$. The quantum yield of Cl atoms was not determined in that work. Subsequently, Lawrence, *et. al.*,[6] reported that the quantum yield of Cl was below $5 \times 10^{-4}$ between 359 and 368nm, and that the $Cl + O_2$ channel had a negligible impact on the balance of atmospheric ozone. Quite recently, however, Bishenden and coworkers[7] disagreed, concluding that Cl atoms are formed upon single photon excitation of OClO near 362nm with a quantum yield of $0.15 \pm 0.1$. The Cl atom yield at other wavelengths was not explicitly reported, but a structured Cl REMPI action spectrum was presented[7] for the wavelength range 355nm-367nm.

Figure 1 shows the energetics of OClO decomposition.[10] At all wavelengths, three electronic states of $O_2$ are thermodynamically possible. In none of the experiments reported to date[2,7] was the electronic state of the $O_2$ determined. In fact, in no case was $O_2$ directly observed-- all experimental evidence has been based on observation of the Cl atom alone. This leaves open the possible involvement of other sources of Cl signal, such as photodissociation of the dominant ClO product.

Using the technique of photofragment translational energy spectroscopy,[11] we find that $Cl + O_2$ is formed from single photon absorption by OClO, but the yield is only appreciable (>1%) at wavelengths ***longer*** than 390nm. Unlike the previous measurements,[2,7] we have observed both momentum matched Cl + $O_2$ products, and the quantum yields are based on direct measurements under well defined single photon conditions. Translational energy measurements show that $O_2$ is definitely formed in the ground ($^3\Sigma^-_g$) state and there is very strong evidence for a substantial fraction in the first excited ($^1\Delta_g$) state.

The OClO molecule has a structured absorption spectrum[1,12] corresponding to progressions in ($v_1$,0,0), ($v_1$,1,0), ($v_1$,0,2), and ($v_1$,1,2) of the excited $^2A_2$ state. (Fig. 2) Despite a dissociation lifetime of many vibrational periods,[3] we observe mode specificity in the branching ratios for the two channels. The yield for Cl + $O_2$ is always greatest (up to 3.9%) under OClO absorption peaks associated with combinations of symmetric stretching with symmetric bending ($v_{1,}$,1,0) motion. Although the yield is only slightly smaller from pure symmetric stretching modes ($v_1$,0,0), excitation at nearly the same energy to a symmetric stretching + asymmetric stretching mode ($v_1$,0,2) leads to a tenfold decrease in the Cl + $O_2$ yield. Mode specific behavior is also seen in the ClO vibrational energy distributions which are strongly dependent on the initial vibrational state of the OClO molecule.

## Experimental

The experiments were conducted using a molecular beam apparatus equipped with a rotatable molecular beam source and fixed detector.[11] The unfocussed output from an excimer-pumped Lambda-Physik FL2002 dye laser was crossed at 90 degrees with a seeded supersonic molecular beam containing 10-20% OClO in helium or argon. In some experiments, a continuous beam was formed by expanding ~150 Torr of the mixture through a 0.007" dia. nozzle heated to ~80°C. Experiments were also conducted using a room temperature pulsed nozzle (0.020" dia.) and a pressure of 1 atm. The OClO was generated *in-situ* by flowing a 5-10% $Cl_2$/inert gas mixture through a U-tube packed with glass beads and $NaClO_2$, as described elsewhere.[2,12] The $Cl_2$ impurity in the beam, measured using a mass spectrometer, was found to be negligible provided that the $NaClO_2$ is not too dry-- apparently the reaction $Cl_2(g) + 2NaClO_2(s) \rightarrow 2NaCl(s) + 2ClO_2(g)$ requires the presence of some moisture.

A small fraction of the photodissociation products recoiled away from the molecular beam axis into an electron bombardment ionizer located 36.7 cm away from the interaction region.[11] Ions were extracted into a quadrupole mass filter and detected by a Daly 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. The product time-of-flight spectra were analyzed using an updated version of the forward convolution program CMLAB2, as described previously.[11]

## Results and Discussion

Under all absorption peaks between 350nm and 475nm, the dominant products (>96%) from dissociation of OClO are $ClO(^2\Pi)$ + $O(^3P)$. Product time-of-flight (TOF) spectra were recorded at $Cl^+$, $ClO^+$, $O^+$, and $O_2^+$. We observed $Cl^+$ daughter ions from fragmentation of ClO (from ClO + O) in the electron bombardment ionizer, and $Cl^+$ parent ions from the Cl + $O_2$ channel. As predicted from the Newton diagram (Fig. 3), both photodissociation channels can be seen by monitoring $Cl^+$ and can be distinguished by their TOF spectra. Even if the $O_2$ fragment is formed in v=5 of the $^1\Sigma^+_g$ state (the second electronically excited state), the recoil velocity of its Cl atom partner will be greater than the velocity of ClO (v=0) from the ClO + O channel.

Time-of-flight spectra recorded at $Cl^+$ (m/e=35) are shown in Figure 4 for three neighboring excitation wavelengths, corresponding to the (5,1,0), (4,0,2), and (5,0,0) vibrational levels of OClO ($A^2A_2$). The angle between the molecular beam and detector was 20°, and a 20% OClO/He mixture was expanded through a room temperature pulsed nozzle. The slower peak in the TOF spectrum was identical to that seen in the $ClO^+$ TOF and results from ClO fragmentation in the ionizer. The fast peak is due to Cl from the Cl + $O_2$ channel. Our assignments are confirmed by observation of the respective momentum matched O and $O_2$ fragments (Fig 5). Based on linewidth measurements[3], it is known that the OClO dissociation lifetime is many picoseconds at these wavelengths. Thus, unless the laser was tuned very close to the origin[1] of a vibrational band, we found that rotating the laser polarization using a double fresnel rhomb had no effect on product intensities, since the parent molecule rotated at least several times before dissociating. All data reported here was obtained with the dye laser tuned 4-5 $cm^{-1}$ to the red of the bandhead positions reported in Ref. 1. Although our laser does not provide rotational resolution, ($\Delta E \sim 0.2cm^{-1}$) , we see only minor effects on the shapes of the TOF or Cl + $O_2$ yields upon tuning across the rotational envelopes of given vibrational levels of OClO.

The translational energy distributions for both channels from excitation of the (5,1,0) band are shown in Figure 6. They are based on data shown in Figures 4 and 5, as well as other data (not shown) obtained at other angles between the molecular beam and detector.[13] The fastest component of the Cl + $O_2$ channel, with $E_{trans}$ up to ~68 kcal/mole, must correspond to formation of ground state $O_2$ ($^3\Sigma^-_g$). The additional feature peaking at ~33 kcal/mole is very strongly suggestive of formation of excited $O_2$ ($^1\Delta_g$). As shown in Fig. 4, the shapes of the Cl + $O_2$ times-of-flight (and $O_2$ internal state distributions) are not strongly dependent on the initial OClO vibrational level. The ClO internal state distribution, on the other hand, is very sensitive to the initially prepared OClO state. Structure due to vibrational excitation of the ClO($^2\Pi$) product is quite well resolved, particularly when its O atom recoil partner was monitored (Fig. 5). Analysis is currently under way to extract approximate vibrational energy distributions as a function of OClO vibrational state.[13]

The branching ratios for formation of $Cl+O_2$ relative to ClO+O were calculated from the fits to the experimental data at m/e=35($Cl^+$), accounting for the different Jacobian factors for the LAB→CM transformation for each channel. One additional factor that is required in the analysis is the relative detection sensitivity for ClO and Cl at m/e=35 ($Cl^+$). This quantity was determined experimentally in a separate experiment. We monitored the equal yields of Cl and ClO from ClOCl photodissociation at 423nm.[13,14] The fast peak in the m/e=35 TOF resulted from Cl and the slower peak was from fragmentation of ClO-- their contributions led to a very accurate measure of the relative detection sensitivity for the two fragments.[15] The measured branching ratios were converted to absolute yields by assuming that $\Phi_{diss} = \phi_{Cl+O2} + \phi_{ClO+O} = 1.0$.[16] Our absolute Cl + $O_2$ yields should be accurate to ±20%.

Our results indicate that the yield for $Cl+O_2$ has a maximum of 3.9 ± 0.8% under the peak near 404nm dropping to <0.2% under peaks at wavelengths below 370nm. The Cl + $O_2$ channel is observed at longer wavelengths, but is weaker-- the yield under the (4,0,0) band at ~423nm is ~1.2%. Our conclusion that the yield is negligible below 370nm is in qualitative agreement with Lawrence,[6] who could not actually see Cl + $O_2$, but placed an upper limit of 0.05% below 368nm. Extensive averaging would be required in our experiment to further reduce our upper limit of 0.2% for $\lambda < 370$nm. All previous experimental efforts[3-7] have focussed on a wavelength range near 365nm, apparently because early matrix isolation experiments[18] found that the formation of ClOO by irradiation of OClO was favored using filters transmitting at that wavelength. We have not been able to observe any $Cl+O_2$ at 362nm, the wavelength peak for the Cl signal observed by Vaida,[2] and Bishenden.[7] This is not surprising since 362nm corresponds to a wavelength *minimum* in the OClO absorption spectrum (Fig. 2).[1,12] Absorption at 362nm is primarily from high rotational levels of OClO, decreasing with decreasing cell temperature[12] or with supersonic cooling in the molecular beam.[1] Absorption to electronic states other than OClO($^2A_2$) is thought to be unlikely in this wavelength region.[1] Even the dominant, usually very strong ClO + O signal was relatively weak at 362nm in our molecular beam experiment.

Bishenden, et al,[7] obtained a value of 15±10% for the Cl + $O_2$ channel at 361nm, based on comparisons of Cl REMPI spectra from $Cl_2$ and OClO. Their REMPI spectrum showed some similarity to the Cl spectrum reported earlier by Vaida.[4] The chief experimental differences are that in Bishenden's work, a tunable laser was employed for excitation and a second fixed at the 2+1 Cl REMPI resonance (rather than one laser wavelength for both pump + probe), and a gas cell was used instead of a molecular beam. In both cases, however, the highest Cl signal intensity fell at 362nm,[4,7] an OClO absorption *minimum*.[1,12] It is important to note that the strong $ClO^+$ peaks observed earlier by Vaida at 355.54, 357.10, 358.78, 360.20, 362.03, 363.83, and 365.10nm were attributed to two photon $ClO(C^2\Sigma \leftarrow X^2\Pi)$ resonances.[4] The Cl REMPI action spectrum of Bishenden also has peak positions falling very close to those listed above, but the peaks are broader, the peak at 363.83nm is a shoulder, and that at 365.10nm is too weak to observe.[7] Although a Cl quantum yield of 0.15 was obtained at 361nm,[7] our simple calculations[19] employing Bishenden's spectra[7] and the known OClO[12] and $Cl_2$ absorption[20] cross sections lead to a value of ~1.0 at 362 nm. This behavior, not noted by the original authors, arises because their action spectrum does not follow the known[1,12] OClO absorption spectrum. A 2nm shift of their spectrum to the blue cannot resolve the problem since Vaida also observed the maximum Cl signal at 362nm.[4] The observed features, if not due to two photon $ClO(C^2\Sigma \leftarrow X^2\Pi)$ resonance structure, cannot be explained by any known OClO absorption features. In our experiment at longer wavelengths, the signal levels for both ClO + O and Cl + $O_2$ sensibly track with the OClO absorption spectrum. Near 362nm, although we do not see Cl + $O_2$, we find that the ClO + O product wavelength dependence is consistent with the known OClO absorption profiles.[1,12] The possibility of excitation of nascent $ClO(X^2\Pi)$ by a two photon transition to the $(C^2\Sigma)$ state, followed by photodissociation to Cl + O and then 2+1 Cl REMPI, was not considered by the original authors but is strongly suggested by their spectrum.

It is interesting to compare our gas phase results with the matrix results of Arkell, et al.[18] We observe a significant yield (>1%) of Cl + $O_2$ only at wavelengths longer than 390nm, whereas they found that ClOO is favored in the matrix by irradiation at ~365nm.[18] This suggests that our observation of the Cl + $O_2$ channel under isolated gas phase conditions is probably unrelated to observation of ClOO in the matrix experiments. The mechanism for ClOO formation, postulated by the original authors,[18] appears more likely than mechanisms suggested in more recent reinterpretations[3-5,21,22] of their data: Photodissociation near 365nm leads to formation of ClO + O but due to the matrix cage effect, back reaction of the nascent O atom leads to ClOO. Back reaction in the matrix cage will be facile because the $ClO(^2\Pi)$ + $O(^3P)$ electronic states correlate directly with ClOO (A',A").[21] The "enhancement" in yield of ClOO in the matrix by irradiation near 365nm,[18] (rather than at 220nm$<\lambda<$350nm or 450nm$<\lambda<$590nm) probably results from the OClO absorbing most strongly in that region.[1,12,22]

Previous discussion regarding OClO → Cl + $O_2$ has centered on a photoisomerization mechanism involving an intermediate ClOO radical.[1-5,7,21,22] However, a mechanism formally involving isomerization of OClO to ClOO followed by simple bond rupture does not appear to be consistent with our observations. The large translational energy release that we observe in the recoiling Cl + $O_2$ is characteristic of a concerted unimolecular decomposition from a highly constrained transition state, followed by strong repulsion between the products. This transition state is probably best considered to be an OClO molecule with a strongly compressed bond angle and only some distortion from $C_{2v}$ symmetry. This is consistent with the Cl-O antibonding and O-O bonding nature of the $2b_1$ orbital into which the electron is excited, resulting in a decrease in OClO bond angle from 117 to $\sim 107^0$, and increase in Cl-O bond length from 1.47 to 1.62Å.[21] Our observation that symmetric stretching + symmetric bending excitation promotes the Cl + $O_2$ channel strongly supports a mechanism involving concerted decomposition from a transition state geometry close to $C_{2v}$. The region of the Cl + $O_2$ potential energy surface corresponding to the Cl-OO isomer represents a very shallow minimum with $D_o$(Cl-OO) = 4.76±0.49 kcal/mol[23] and $\Theta_{Cl\text{-}OO} \sim 110°$.[18,21] In the absence of a large torque on the O=O molecule, the newly born Cl atom will be near the $C_{2v}$ axis of OClO, perpendicular to the O=O bond axis, corresponding to $\Theta_{Cl\text{-}OO} < 70°$. Since the Cl-$O_2$ interaction at this angle is repulsive,[21] the Cl-$O_2$ "isomer" will not exist for much more than one vibrational period. Instead, strong product repulsion leads to a large Cl +$O_2$ recoil energy of up to ~68 kcal/mol.

## Conclusions

We have clarified a number of questions regarding the formation of Cl + $O_2$ in the collision free photodissociation of OClO. Our results indicate that the yield is only appreciable (>1%) above 390nm. For a given energy, the yield of Cl + $O_2$ is always slightly greater under those lines corresponding to excitation of the symmetric bending motion, but is much smaller when exciting an asymmetric mode. The decrease in yield at shorter wavelengths or with asymmetric vibrational excitation likely results from faster predissociation to ClO + O. Suggested gas phase isomerization of OClO to ClOO, based on the earlier matrix isolation results of Arkell, *et al.*,[18] appears to be inappropriate. Although a substantial amount of $O_2$ is formed in the ground electronic state, there is strong evidence for a comparable yield for $O_2(^1\Delta)$, the total reaching a maximum of 3.9±0.8% near 404nm. Further details regarding the mode specificity in the dynamics, complete yields of Cl + $O_2$ as a function of wavelength, and approximate ClO vibrational energy distributions will be presented in a forthcoming article.[13]

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sensitive to its vibrational level for v' = 1-5.

16. Fluorescence observed at longer wavelengths (Ref. 17) should be negligible at these energies.
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19. We used the following room temperature values from Refs. 7, 12, and 20: 362nm- $I_{Cl/OClO}:I_{Cl/Cl2} \sim 10$ ., $\sigma_{OClO}=2.4\text{x}10^{-18}\text{cm}^2$; $\sigma_{cl2}= 1.2\text{x}10^{-19}\text{cm}^2$, $\phi_{Cl/Cl2}= 2.0$
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**Figure Captions:**

Fig.1: Energy level diagram for OClO and possible photodissociation products.

Fig.2: OClO absorption spectrum (204K), from Ref. 12. Vibrational assignments from Ref. 1.

Fig.3: Newton diagram in velocity space for Cl-containing fragments from OClO photodissociation at 404nm. Arrow denotes initial OClO beam velocity, and circles are calculated recoil velocities for formation of ground vibrational state fragments.

Fig.4: Product time-of-flight spectra (20°) recorded at m/e= 35 ($Cl^+$) from indicated OClO vibrational levels. Inset shows expanded vertical scale (x15) to reveal structure in Cl + $O_2$ channel. Cl+$O_2$ yields are also indicated. • • • • - Experimental Data. —— -Optimized fit.

Fig.5: Time-of-flight spectra (40°) for the $O_2$ and O atom channels recorded at m/e=32 ($O_2^+$), and m/e= 16 ($O^+$), from (5,1,0) level. Contribution to $O^+$ from fragmentation of $O_2$ is negligible and contribution from ClO is broad peak at T=350-600$\mu$sec.
• • • • - Experimental Data. —— - Optimized fits based on Fig. 6.

Fig.6: Translational energy distributions for Cl($^2$P) + $O_2$ and O($^3$P) + ClO channels from (5,1,0) level. The calculated maximum relative translational energies for production of internally excited diatomics are indicated.

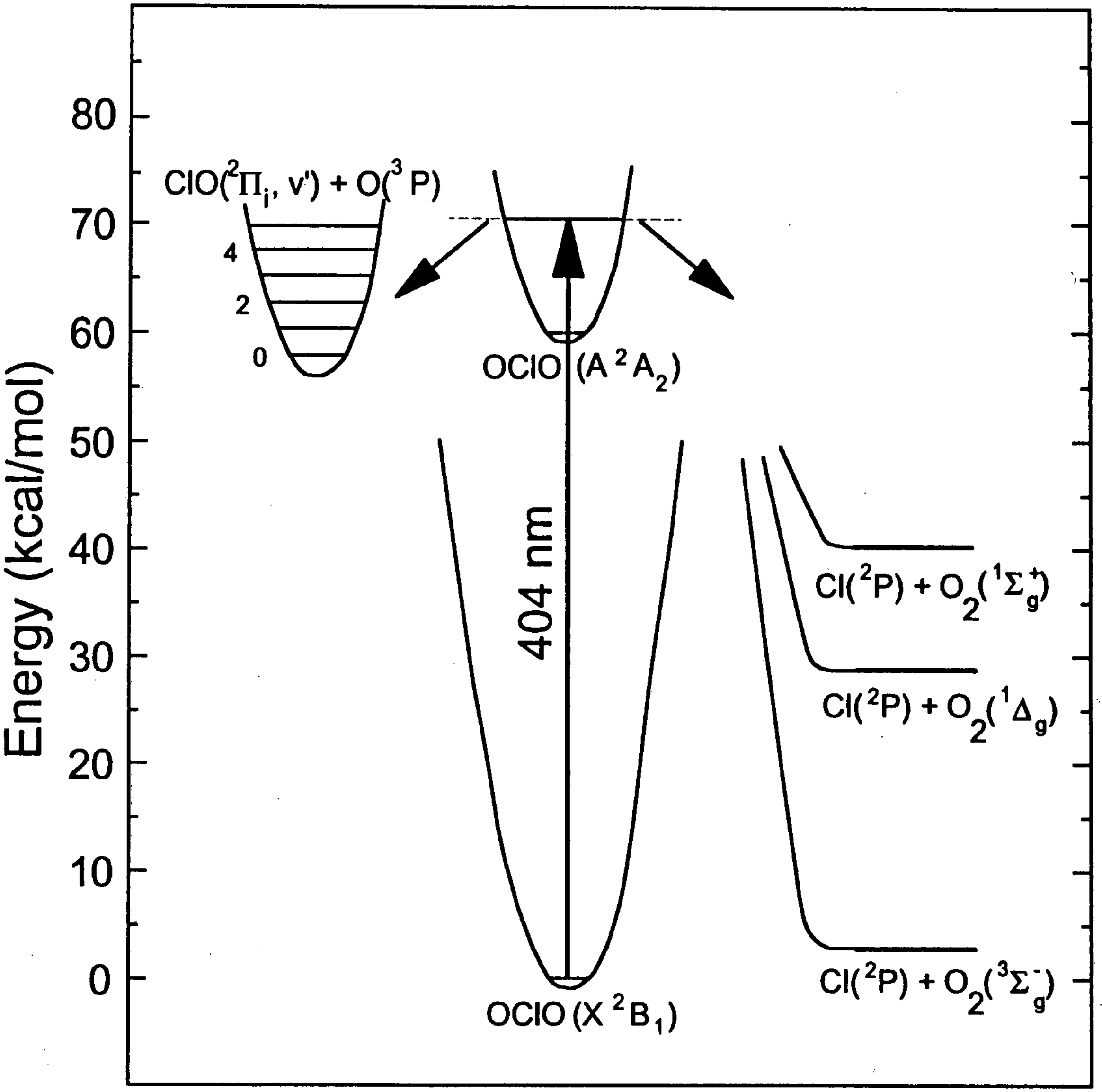
Energy (kcal/mol)
80
70
60
50
40
30
20
10
0
$ClO(^2\Pi_i, v') + O(^3P)$
4
2
0
$OClO\ (A\ ^2A_2)$
404 nm
$OClO\ (X\ ^2B_1)$
$Cl(^2P) + O_2(^1\Sigma_g^+)$
$Cl(^2P) + O_2(^1\Delta_g)$
$Cl(^2P) + O_2(^3\Sigma_g^-)$

Fig. 1

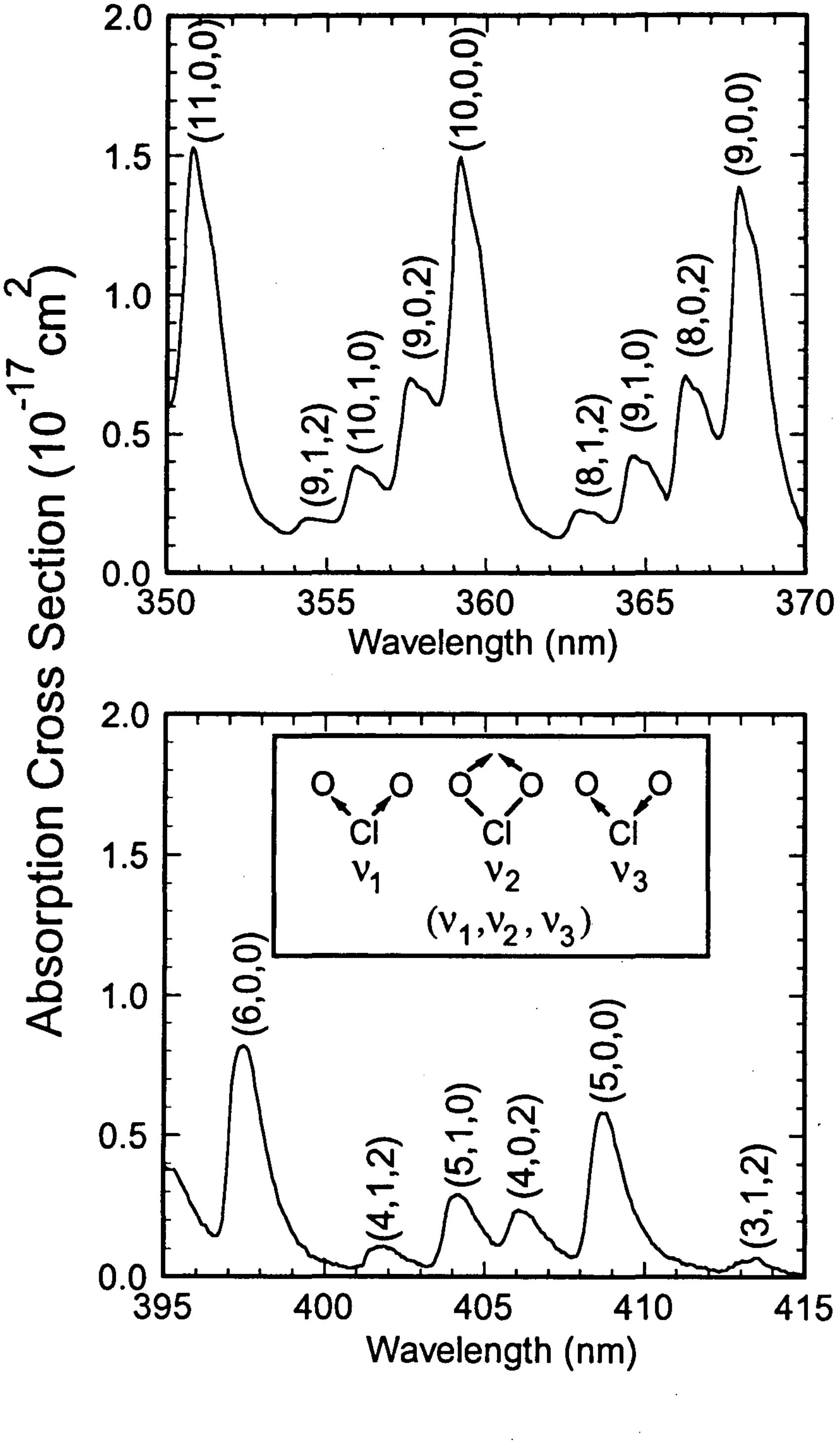
Absorption Cross Section ($10^{-17}$ cm$^2$)
2.0
1.5
1.0
0.5
0.0
350
355
360
365
370
Wavelength (nm)
(11,0,0)
(9,1,2)
(10,1,0)
(9,0,2)
(10,0,0)
(8,1,2)
(9,1,0)
(8,0,2)
(9,0,0)
2.0
1.5
1.0
0.5
0.0
395
400
405
410
415
Wavelength (nm)
O O Cl $\nu_1$
O O Cl $\nu_2$
O O Cl $\nu_3$
($\nu_1$,$\nu_2$, $\nu_3$)
(6,0,0)
(4,1,2)
(5,1,0)
(4,0,2)
(5,0,0)
(3,1,2)

Fig. 2

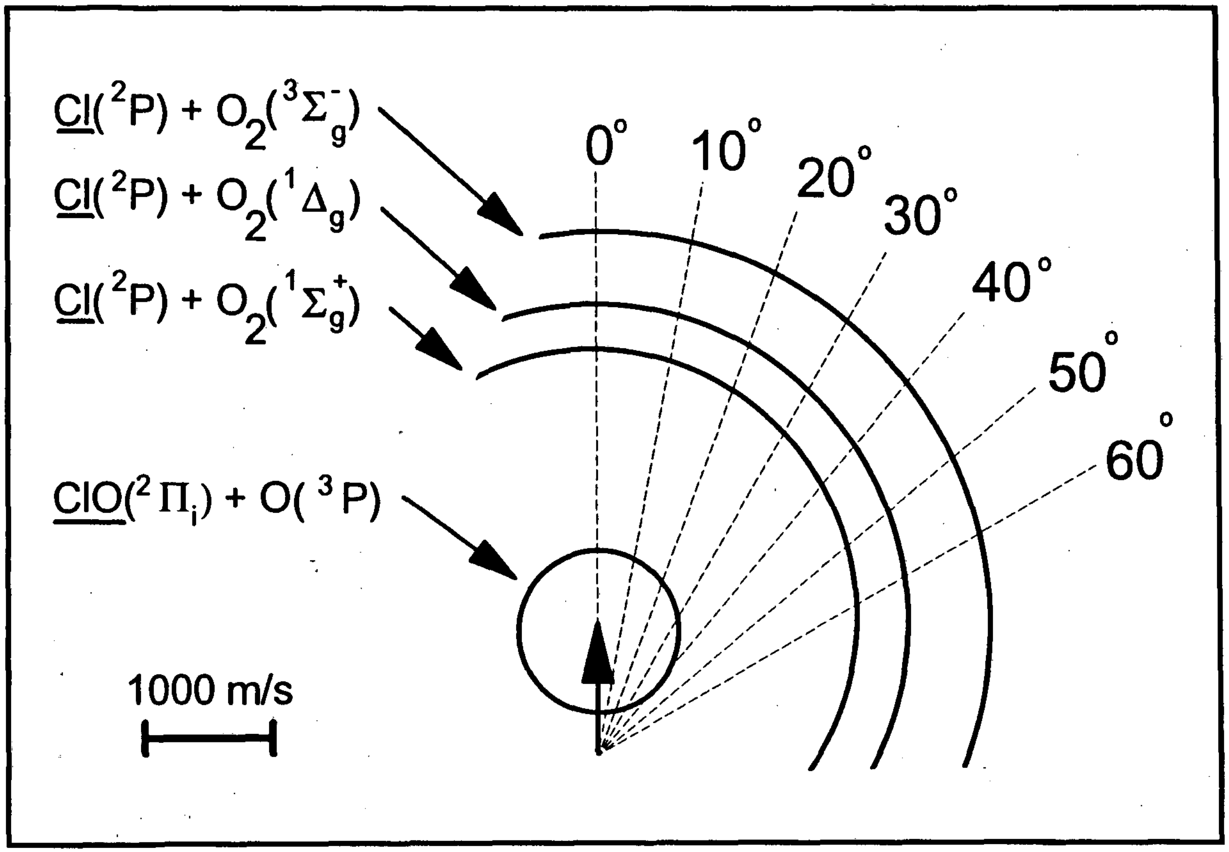
$\underline{Cl}(^2P) + O_2(^3\Sigma_g^-)$
$\underline{Cl}(^2P) + O_2(^1\Delta_g)$
$\underline{Cl}(^2P) + O_2(^1\Sigma_g^+)$
$\underline{ClO}(^2\Pi_i) + O(^3P)$
1000 m/s
0°
10°
20°
30°
40°
50°
60°

Fig. 3

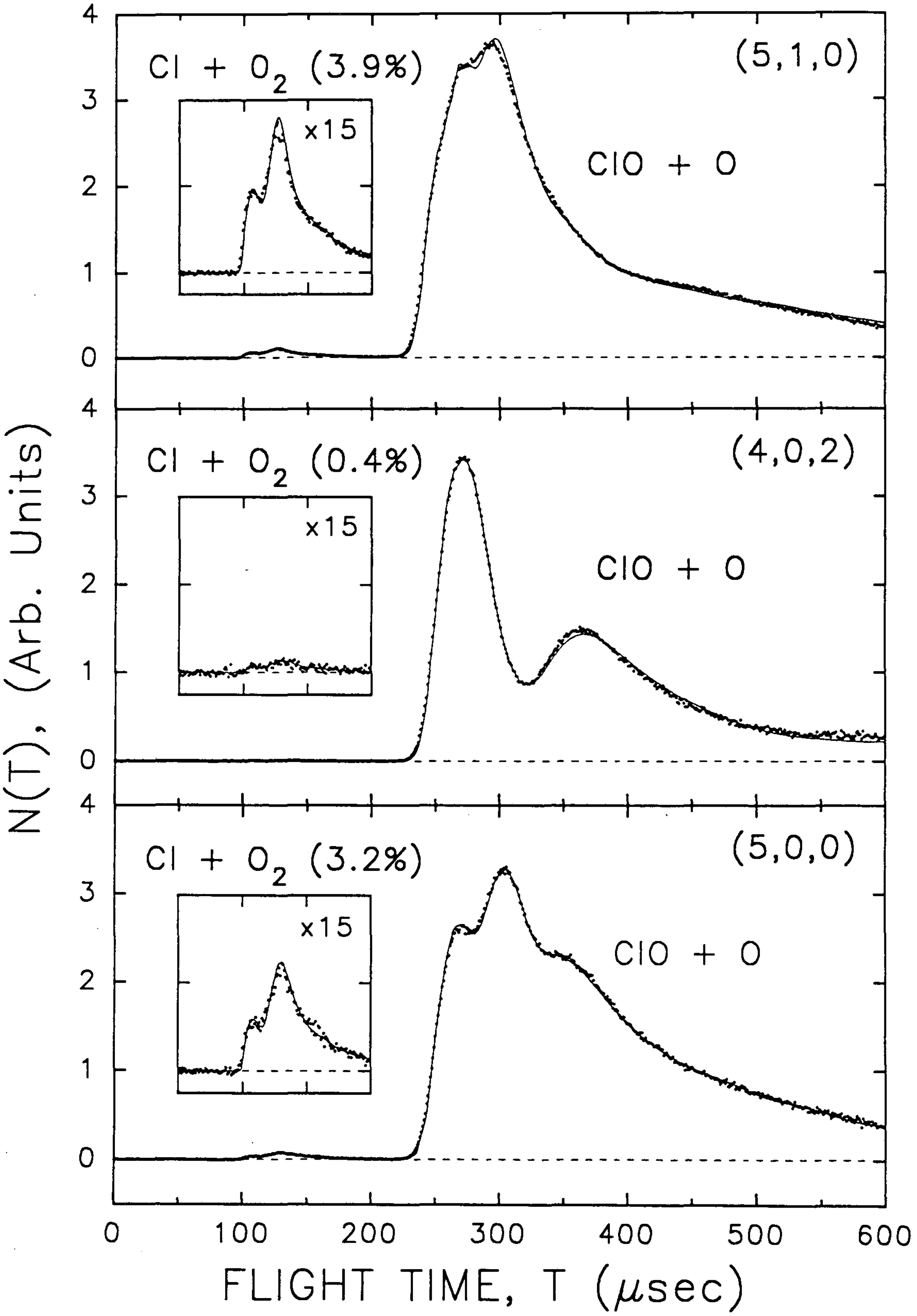
Cl + $O_2$ (3.9%)
(5,1,0)
x15
ClO + O
Cl + $O_2$ (0.4%)
(4,0,2)
x15
ClO + O
Cl + $O_2$ (3.2%)
(5,0,0)
x15
ClO + O
0
1
2
3
4
0
100
200
300
400
500
600
N(T), (Arb. Units)
FLIGHT TIME, T (μsec)

Fig. 4

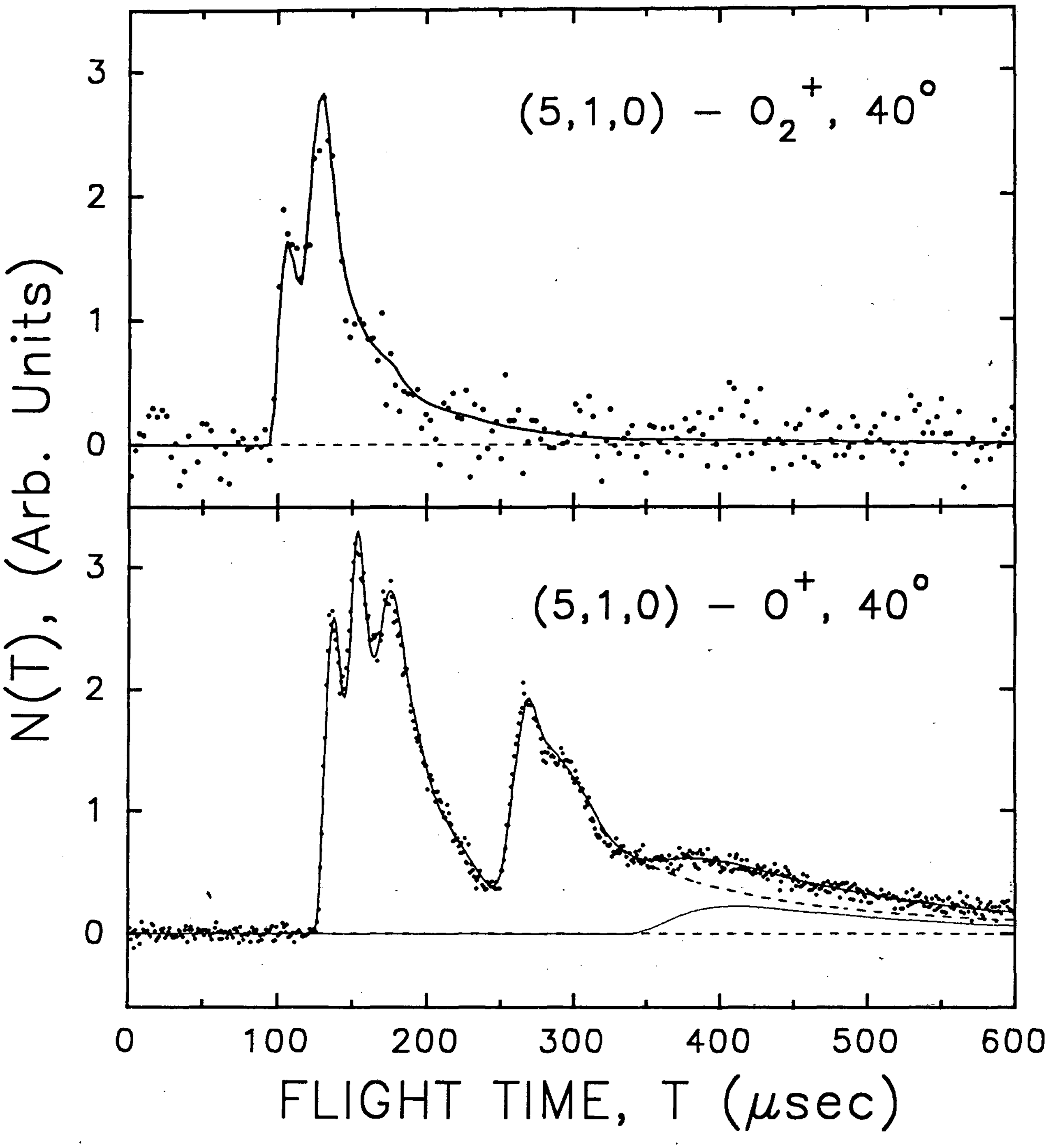
(5,1,0) – $O_2^+$, 40°
(5,1,0) – $O^+$, 40°
N(T), (Arb. Units)
FLIGHT TIME, T (μsec)
0
1
2
3
0
100
200
300
400
500
600

Fig. 5

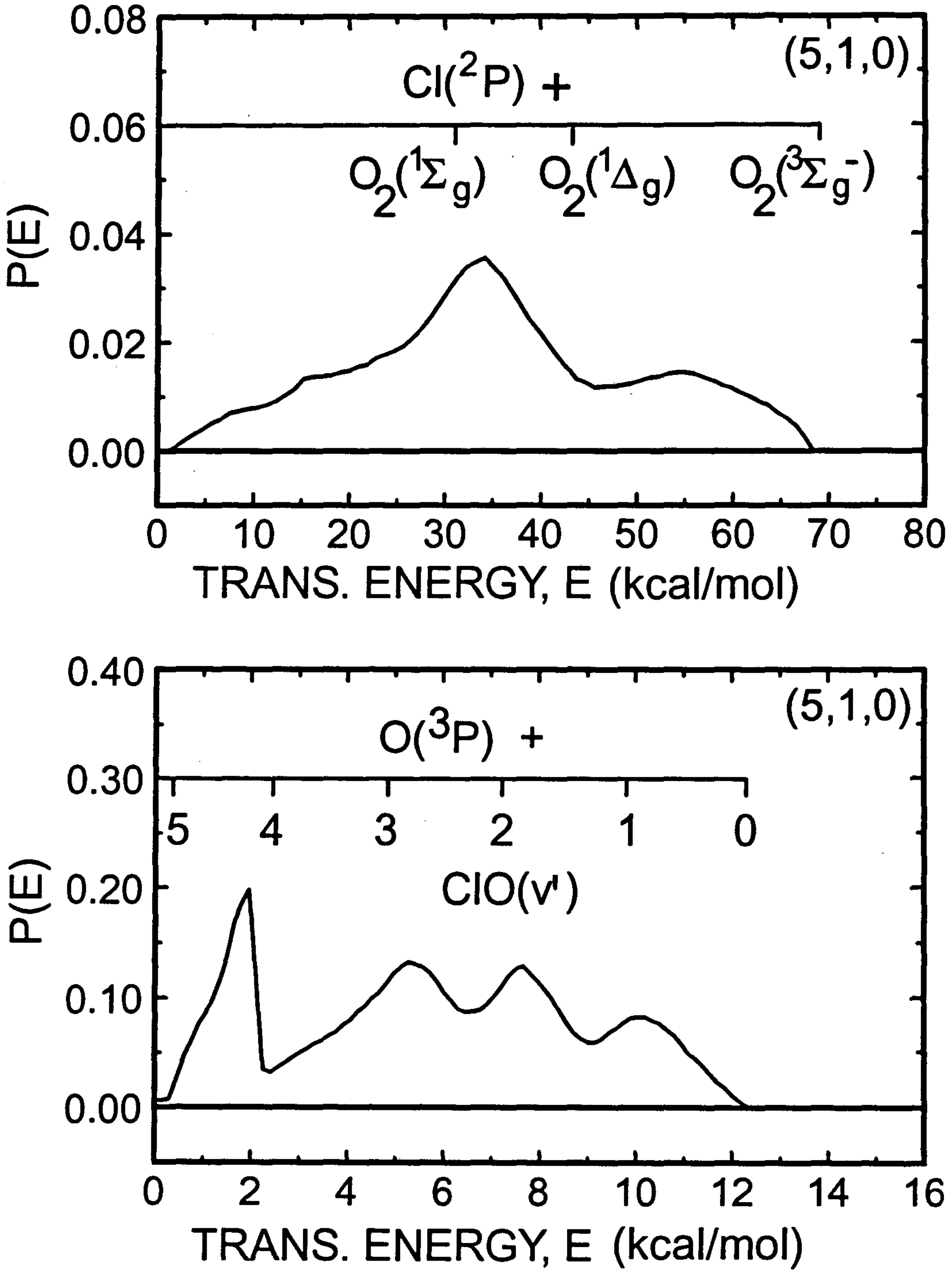
0.08
0.06
0.04
0.02
0.00
P(E)
(5,1,0)
Cl($^2$P) +
O$_2$($^1\Sigma_g$)
O$_2$($^1\Delta_g$)
O$_2$($^3\Sigma_g^-$)
0
10
20
30
40
50
60
70
80
TRANS. ENERGY, E (kcal/mol)
0.40
0.30
0.20
0.10
0.00
P(E)
(5,1,0)
O($^3$P) +
5
4
3
2
1
0
ClO(v')
0
2
4
6
8
10
12
14
16
TRANS. ENERGY, E (kcal/mol)

Fig 6

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