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INFRARED SPECTROSCOPIC STUDY OF Cl₂/O₂ CO-ADSORPTION ON Al(111)

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ABSTRACT

Fourier-transform infrared reflection-absorption spectroscopy (FT-IRRAS) has been used to observe the effects of Cl₂ (O₂) pre-adsorption on the vibrational modes of O (Cl) formed by exposure of Al(111) to O₂ (Cl₂). On clean Al, Cl at surface sites gives rise to a stretching mode at 745-760 cm⁻¹ (depending on coverage), and a second band at 820 cm⁻¹ is tentatively assigned to subsurface Cl. Exposure to O₂ either before or after Cl₂ leads ultimately to a single broad band at a frequency intermediate to those for exposure of the clean surface to either Cl₂ or O₂. The results indicate strong coupling between Al-O and Al-Cl modes and suggest that the two species are intimately mixed during co-adsorption.

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Infrared reflection-absorption spectroscopy (IRRAS) is becoming an important technique for obtaining structural information concerning adsorbates on surfaces. The high resolution ($<5\text{ cm}^{-1}$) attained in many IRRAS experiments, together with the non-destructive character and freedom from a requirement for UHV, make IRRAS potentially useful in studies of complex reactions on surfaces. One such class of surface chemical phenomena in which IRRAS has been usefully applied¹⁻⁵ is "co-adsorption", wherein a pre-adsorbed species influences the subsequent adsorption of a second and vice versa.

This Note reports work aimed at obtaining insight into the mechanism for chlorination of Al and the structure of the O-Cl co-adsorbed phase. IRRAS has already been shown⁶ capable of distinguishing isolated subsurface O from O in oxide islands, on the basis of the resonant frequency ($830\text{ vs }865\text{ cm}^{-1}$) for vibration normal to the surface, and of observing the conversion of isolated to island species with increasing coverage or with annealing. Cl adsorption on Al(111) has been found⁷ to occur at surface sites at low exposure and at subsurface sites at higher exposure. Cl at surface sites gives rise to a broad thermal desorption peak at about 200°C . Pre-adsorbed O inhibits formation of the subsurface phase but does not greatly affect Cl adsorption at surface sites. However, the techniques used in ref. 7 - Auger spectroscopy, work function measurement and temperature programmed desorption - do not permit direct observation of distinct Cl and O species. IRRAS, on the other hand, provides a bond-specific probe with which different species can be distinguished during the chemisorption process.

Most of the experimental details have been given previously^{6,7}. The chamber was equipped with KBr windows according to the design of Hollins and Pritchard⁸. Radiation striking the sample was p-polarized and incident at $\sim 86^\circ$ with an angular spread of $\pm 4^\circ$. A Mattson Sirius 100 FTIR system was used with a liquid N₂-cooled wide-band MCT (HgCd_xTe_{1-x}) photoconductive

detector providing a usable signal-to-noise ratio (SNR) down to 600 cm^{-1} . 2000 bi-directional scans (20 min. total scan time) were averaged at 8 cm^{-1} resolution, and four-fold zero-filling of the double-sided interferograms was used to give a point spacing of 1 cm^{-1} . Data obtained at 4 cm^{-1} resolution showed no additional structure. Spectra were recorded for the clean surface and after each successive gas exposure, and the quantity $\delta R/R \equiv (R_{\text{ex}} - R_0)/R_0$, where R_{ex} (R_0) is the reflectance of the exposed (clean) surface, was computed. The noise level corresponded to $\delta R/R \approx 1 \times 10^{-4}$ except toward the end of the detector range where it increased several fold. All spectra are shown "as recorded" (no smoothing). The optical path was purged with dry N_2 to reduce interference in the $640\text{--}690\text{ cm}^{-1}$ range from atmospheric CO_2 . All experiments were done at a sample temperature of $30\text{--}38^\circ\text{C}$. Exposures are in Langmuirs (L), where $1\text{ L} = 10^{-6}\text{ torr-sec} = 3.59 \times 10^{14}\text{ O}_2/\text{cm}^2$ or $2.41 \times 10^{14}\text{ Cl}_2/\text{cm}^2$, and are based on ionization gauge readings uncorrected for O_2/N_2 and Cl_2/N_2 relative sensitivities. Auger analyses were performed before and after each series of IRRAS experiments. Following large Cl_2 exposures on the clean surface a small level of O contamination (but no other impurity) was detected⁷.

FT-IRRAS results for O/Al(111) for O_2 exposures of 5-50 L showed only the subsurface O band, with a maximum at $815\text{--}860\text{ cm}^{-1}$ depending on coverage, in agreement with previous⁶ data obtained using tunable diode lasers. No additional structure was observed at the present higher resolution (8 vs 20 cm^{-1}). As before⁶, the surface O mode - seen in EELS (electron energy-loss spectroscopy) at $550\text{--}690\text{ cm}^{-1}$, depending on coverage and substrate temperature during exposure (ref. 6 and work cited) - was not detected. For a very large O_2 exposure (several thousand L) the p-polarized $\delta R/R$ peak occurs at about 930 cm^{-1} , close to the bulk Al_2O_3 LO phonon frequency⁹ of 950 cm^{-1} .

The only available vibrational data for a halogen on clean Al is the EELS work of Chen et al.¹⁰ for dissociative adsorption of CH_3I on Al(111)

which indicates an Al-I mode at 335 cm^{-1} . Presumably, because of its large size, I occupies only surface sites. Assuming a purely quadratic potential, equal Al-Cl and Al-I force constants and a rigid surface plane one would expect the corresponding Al-Cl mode at 640 cm^{-1} , i.e., an increase by a factor of $(M_I/M_{Cl})^{1/2} = 1.91$. Surface enhanced Raman data¹¹ for halogen ions on Ag and Au electrodes show an M-Cl/M-I ($M = \text{Ag, Au}$) frequency ratio of 2.1-2.2, suggesting a larger force constant for the M-Cl bond. This leads to a rough estimate of $700\text{-}740\text{ cm}^{-1}$ for the surface Al-Cl vibration. Recent EELS work by Ng et al.¹² on the electron-stimulated decomposition of $(\text{CF}_2\text{H})_2\text{O}$ on oxidized Al(111) suggests the Al-F mode to lie at 870 cm^{-1} . Scaling this value by $(M_{Cl}/M_F)^{1/2} = 1.36$ gives an Al-Cl mode at 640 cm^{-1} , identical to the uncorrected estimate based on the Al-I energy. However, the effect of adsorbed C and O on the reported Al-F frequency is not known.

The results for exposure of the clean surface to Cl_2 are shown in Fig. 1. At the lowest exposure a single band (in the accessible range) is observed at about 745 cm^{-1} which shifts to about 760 cm^{-1} at 20 L and reaches a nearly constant intensity. The position of this band agrees reasonably well with the estimate for the surface Al-Cl mode obtained above, and briefly annealing the sample to 200°C causes nearly complete elimination of this band. The dependence of the IRRAS data on Cl_2 exposure and on annealing, as well as the mode frequency, are all consistent with Cl adsorption at surface sites. At the lowest exposures a shoulder is seen on the high-energy side of the 745 cm^{-1} band. This feature develops into a peak at about 820 cm^{-1} and continues to grow slowly in intensity (but not shift significantly) up to 80 L (the highest exposure used here). This mode is considerably higher in energy than would be expected for the surface Al-Cl stretch, and its dependence on Cl_2 exposure is consistent with adsorption at subsurface sites. However, assignment of this band must be done with caution because of sensitivity of the $780\text{-}840\text{ cm}^{-1}$ region of the Cl/Al(111) spectrum to small

amounts of O (see below).

For a mode frequency of 745 cm^{-1} an Al- ^{35}Cl - Al- ^{37}Cl isotopic shift of 20 cm^{-1} with a 3/1 relative intensity (relative abundance) for the higher frequency (lighter isotope) would be expected. The spectra show no clear indication of such a splitting. This might result from dipole coupling¹³ between the Al- ^{35}Cl and Al- ^{37}Cl modes, the uncoupled ("singleton") frequencies of which are separated by less than the linewidth. Such interaction is known^{13,14} to transfer intensity from the lower to the higher energy mode and in this case might reduce the Al- ^{37}Cl intensity below the detection limit. Verification of this effect would entail recording spectra for a series of $^{35}\text{Cl}_2/^{37}\text{Cl}_2$ mixtures of varying relative concentration. Isotopically pure Cl_2 was not available during the course of these experiments. At very low Cl coverage, for which dipole coupling is at a minimum, the SNR is too low to permit observation of a weaker Al- ^{37}Cl component. Mixed isotope experiments would also aid in determining the relative contributions of chemical and dipole coupling effects to the $745\text{-}760\text{ cm}^{-1}$ coverage dependent shift¹³.

Figs. 2 and 3 show the spectra obtained for exposure to Cl_2 (O_2) followed by exposure to O_2 (Cl_2). The results are not simply sums of O/Al and Cl/Al spectra, indicating that the surface cannot be described as a "phase separated" composite of chlorinated and oxidized patches and that a model based on a mixture of interacting Al-O and Al-Cl bonds is more appropriate. The effects of the interaction are seen clearly when a surface pretreated with one species (even at high exposure) is given a small exposure of the other. In all cases significant changes in band intensity and position occur.

The simplest situation to discuss is that of Cl_2 exposure following 50 L O_2 [Fig. 2(a)]. The O_2 pre-exposed surface (ref. 6 and work cited) is "saturated" in the sense that all energetically favorable O sites are occu-

pied, and further O uptake is very slow. The surface layer is not, however, equivalent to Al_2O_3 since the O vibrational mode, at 850 cm^{-1} , is well below the bulk oxide LO frequency of 950 cm^{-1} (see above), and the Al $\text{L}_{2,3}\text{VV}$ Auger lineshape⁶ shows that not all surface Al sites are fully O-coordinated. Pre-adsorbed O blocks Cl adsorption at subsurface sites⁷ but not at surface sites, which saturate at low Cl_2 exposure. The IRRAS data show that the surface Cl has a significant effect on the subsurface Al-O mode, shifting the peak 10 cm^{-1} to lower energy and causing an approximately two-fold increase in intensity. Further Cl_2 exposure has little or no effect, consistent with Auger data⁷ showing that Cl uptake for this O₂ pre-exposed surface ceases when the surface sites are filled. We envision the resulting system as consisting of a layer of subsurface O underlying a mixed Al-Cl and Al-O surface layer.

A qualitative interpretation of the data in Fig. 2(a) can be formulated with reference to slab-model calculations by Strong et al.¹⁵ for O/Al(111). Their results, obtained using fixed force constants, consider only lattice dynamical effects associated with different O binding sites while ignoring any dependence of valence chemistry on O coverage. They find that the presence of subsurface O causes a shift of about 60 cm^{-1} to higher energy in the mode frequency for surface O. Similarly, for certain subsurface O binding sites, the presence of surface O causes a shift of about 30 cm^{-1} to lower energy for the subsurface mode. These results are consistent with the -10 cm^{-1} shift in the subsurface O mode as surface Cl sites are filled. Note also that the 10 L Cl_2 exposure causes a significant increase in band intensity; whereas, the band resulting from the same Cl_2 exposure on the clean surface [Fig. 3(b)] is barely visible on the scale of Fig. 2(a). Since the Cl Auger intensities are similar in both cases this implies that, in addition to the lattice dynamical effect discussed above, there is a chemical interaction between adsorbed O and Cl leading to an enhancement of

the Al-O dynamic dipole moment.

The situation is more complicated in other exposure regimes [e.g., Figs. 2(b), 3(a,b)] for which both O and Cl occupy both surface and subsurface sites. In this case the possible combinations of chemical and lattice-dynamical effects are complex; however, the data all show evidence for interaction of different species. For example, for a low O₂ pre-exposure [Fig. 2(b)], insufficient for "saturation" as described above, the surface Al-Cl mode is observed at about 735 cm⁻¹. However, the +15 cm⁻¹ shift with increasing Cl coverage seen on the clean Al surface does not occur, indicating that the interaction between adsorbed Cl atoms producing this shift is impeded by the presence of O. For a Cl-covered surface showing clear 760 and 820 cm⁻¹ bands [Fig. 3(a)] addition of O leads eventually to a single broad band at 810 cm⁻¹.

Further insight into the structure of the O+Cl co-adsorbed phase can be obtained from the data in Figs. 2 and 3. Addition of a small amount of O when most of the surface Cl sites are filled [Fig. 3(b)] yields a band at 780 cm⁻¹, intermediate between the low-coverage subsurface O [815 cm⁻¹, Fig. 2(b)] and surface Cl (745 cm⁻¹) energies. Further O₂ exposure, up to 50 L, yields a band very similar in position and intensity to that for 10 L Cl₂ following 50 L O₂ [Fig. 2(a)]. This shows that the distribution of Cl and O between surface and subsurface sites is the same in either case, suggesting that O and Cl do not compete for surface sites. Were this not the case, then a large O₂ pre-exposure would prevent occupation by Cl of those sites populated by a small Cl₂ exposure on the clean surface.

To summarize, we have, first, obtained high-resolution vibrational spectroscopic data identifying a surface Cl mode at 745-760 cm⁻¹ on Cl₂-exposed Al(111). The assignment has been supported by correlation with previous⁷ Auger, work function and temperature programmed desorption results and with vibrational data¹⁰ for I/Al(111). Another band, tentatively

assigned to Cl at subsurface sites, has also been observed at 820 cm^{-1} . Second, the sequential adsorption of Cl at surface then subsurface sites and the lack of competition between Cl and O for surface (as opposed to subsurface) sites has been demonstrated using vibrational spectroscopy to observe directly the formation of distinct Cl species. Third, coadsorption of O and Cl has been shown to yield an intimately mixed phase rather than distinct chlorinated and oxidized patches. The co-adsorption data have been discussed qualitatively, in terms of strongly coupled Al-O and Al-Cl motions, with reference to the results of slab-model calculations¹⁵ for O/Al(111).

We are most grateful to J.E. Butler for the generous loan of the FTIR apparatus, the infrared detector and other equipment and for encouragement during the course of this work. Preliminary FT-IRRAS experiments for $\text{O}_2/\text{Al}(111)$, including the configuring of the optics, were performed by R.L. Rubinovitz. We thank K.B. Koller for help in learning the use of the FTIR hard- and software. This work was supported by the Office of Naval Research.

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1. FT-IRRAS spectra for Cl/Al(111) vs Cl₂ exposure. ($\delta R/R$)_p refers to the fractional change in p-polarized reflectance induced by Cl₂ exposure. The sharp feature at 660 cm⁻¹ arises from atmospheric CO₂, the concentration of which varies slowly with time as a result of imperfect N₂ purging of the optical path.
2. FT-IRRAS spectra for a sequence of Cl₂ exposures for Al(111) pre-exposed to (a) 50 and (b) 10 L O₂. Note compression of ($\delta R/R$)_p scale relative to that of Fig. 1. The vertical lines show the shift, or lack thereof, in the energies of various features in the spectra.
3. Same as Fig. 2 but for a sequence of O₂ exposures for Al(111) pre-exposed to (a) 37 and (b) 10 L Cl₂.

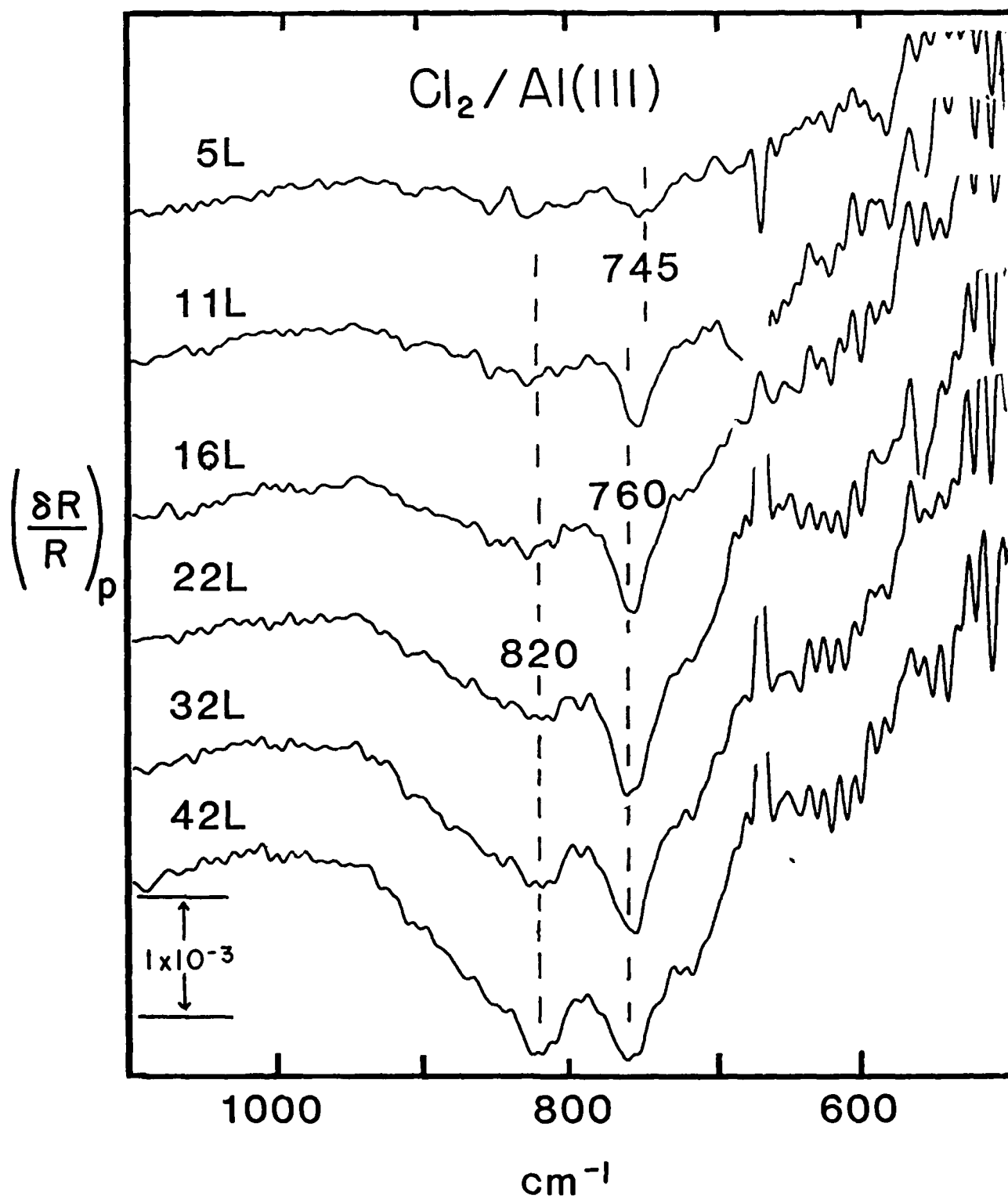


Fig. 1

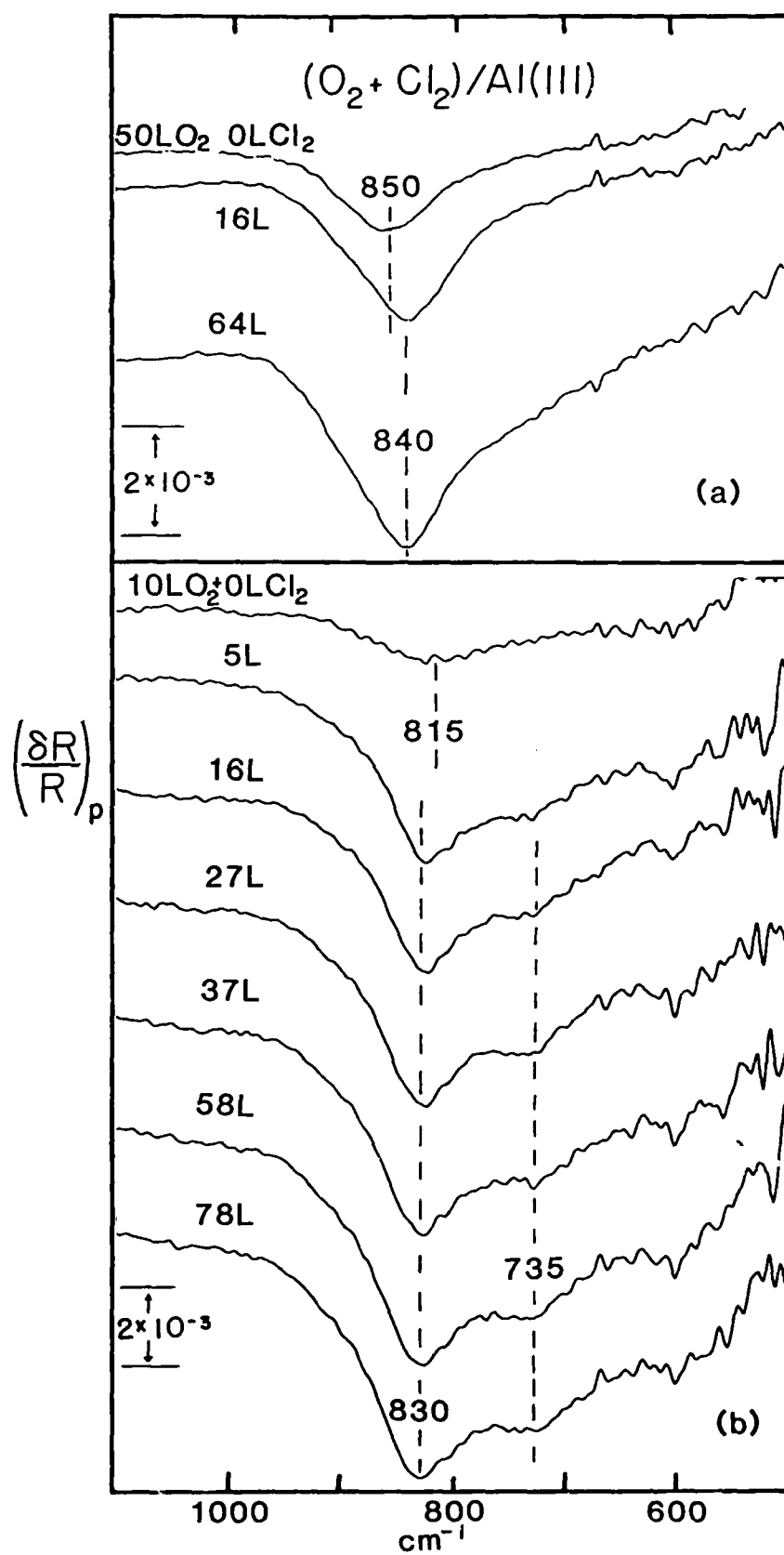


Fig. 2

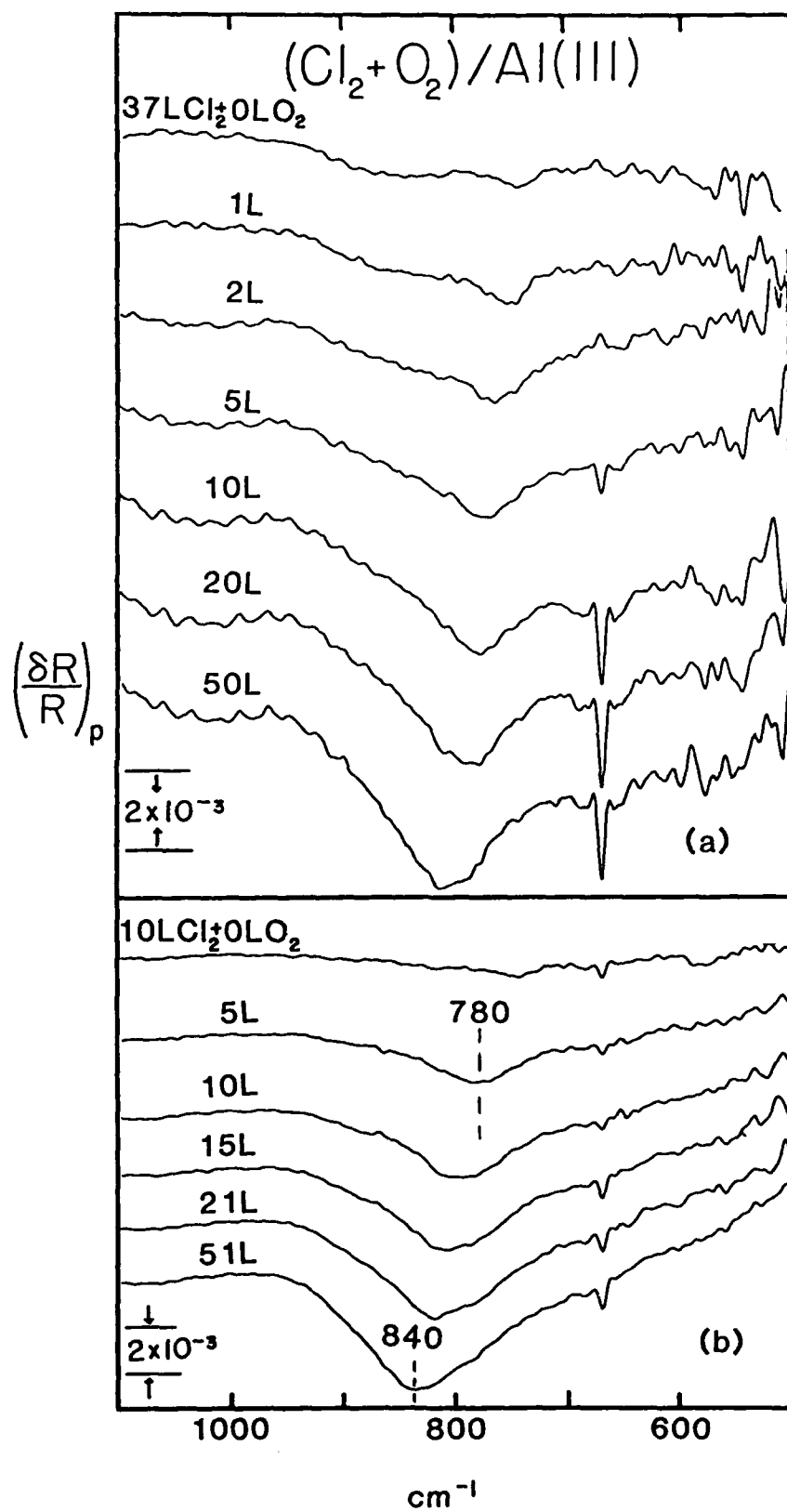


Fig. 3

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