Photon Emission during Chemisorption of Oxygen on Al and Mg Surfaces

Bengt Kasemo
Department of Physics, Chalmers University of Technology, Gothenburg 5, Sweden

(Received 25 March 1974)

Chemisorption of oxygen on Al and Mg was found to cause photon emission with a probability of about 10^{-7} per molecule. The photon intensity was continuously recorded for oxygen exposures 10^{-8}–10^{-1} Torr sec. The intensity is closely related to the chemisorption rate and a rate $<10^{-3}$ monolayer/sec was easily detected. Spectral analysis revealed broad emission bands with maxima at 5100 and 5900 Å for $Al+O_2$ and at 4700 and 5600 Å for $Mg+O_2$.

The energy released in chemical reactions may result in the emission of light (chemiluminescence). In spite of the usually very low probability, 10^{-4}–10^{-9}, for light emission, it has turned out to be a useful way to study the kinetics of chemical reactions in the gas and liquid states.[1] In principle the same process could occur during chemisorption on metal surfaces since the released energy is usually several electron volts per atom. Chemisorptive luminescence has been observed for adsorption of O_2, CO, and NO on W[2] and for O_2 on Si[3] at relatively high gas pressures ($>10^{-3}$ Torr). The light intensity was found to decrease hyperbolically with a time constant of a few seconds.

This Letter presents experimental evidence that spontaneous photon emission occurs during oxygen chemisorption on Al and Mg surfaces at pressures 10^{-9}–10^{-4} Torr, and more important, that this property seems to offer a very sensitive method for investigating chemisorptive processes. The most important observations were as follows: (a) The light intensity is proportional to the oxygen pressure. Its variation with time is closely related, although not necessarily proportional, to the reaction rate. A chemisorption rate of 10^{-3} monolayer/sec was detected with a signal-to-noise ratio of $>10:1$. These properties will be demonstrated for $Al+O_2$. (b) The spectral distribution is characteristic of the reacting system and may be different for different stages of the reaction, as shown for $Mg+O_2$.

The experiments were performed at room temperature in an ion-pumped ultrahigh-vacuum system (base pressure 5×10^{-11} Torr). Al (99.999%) and Mg (99.9%) films were evaporated on the walls of a 6-in.-diam cylindrical cell. A photomultiplier (PM) tube (usually Phillips DVP 56/03) with a light-tight shutter viewed the cell via a Pyrex window. Measurements of light intensity versus time were taken by opening an oxygen (99.999% purity) leak until a desired light signal was detected. The PM-tube signal was recorded by a picoampere meter and fed into a t-y recorder.

Since continuous pressure control was prevented by light from the ion gauge, pressure readings had to be taken intermittently with the light-tight shutter closed. This resulted in a slow, continuous pressure increase during the experiment. When the light signal had decreased to a low level, the oxygen leak rate was increased, thereby increasing the signal. The same procedure with intermittent pressure readings was then repeated. Thus the raw data consisted of two sets of curves: one set for light intensity versus time and another for pressure versus time, both with discontinuities where the leak rate was increased. The data will be presented in the following way: (i) The ordinate designated as I is the light-detector current $J(t)$ divided by pressure $P(t)$, in A/Torr; (ii) the abscissa gives the oxygen exposure,

$$Q(t)=\int_0^t P(t')\,dt',$$

in Torr sec. In this way the discontinuities [in $J(t)$ due to one in $P(t)$] were removed and the same general features of the I-Q curves were reproduced regardless of the pressure during the oxygen exposures. The removal of the discontinuities proves that the light intensity is momentarily proportional to the pressure.

The main experimental errors derive from the pressure measurements and were generally less than 15%. There may, however, be some systematic error due to pressure gradients.

Figure 1 shows the I-Q log-log curve for Al $+O_2$. The data have been obtained at pressures of 10^{-9}–10^{-7} Torr for $Q\lesssim10^{-5}$ Torr sec, 10^{-7}–10^{-5} Torr for $10^{-5}\lesssim Q\lesssim5\times10^{-3}$, and 10^{-5}–10^{-4}

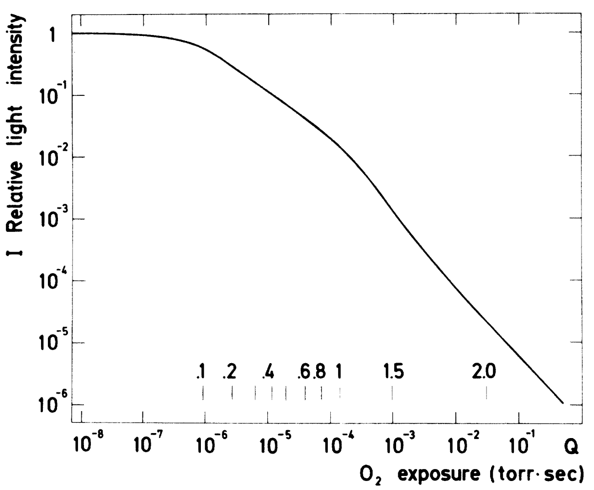

FIG. 1. Emitted light intensity versus oxygen exposure for Al + O_2. Above the Q axis are given the estimated numbers of adsorbed oxygen monolayers.

Torr for $Q \gtrsim 5\times10^{-3}$. To obtain the probability S for photon emission per chemisorbed molecule, the PM tube was calibrated by the photon-counting technique. The number of photons emitted per unit area per second was then calculated assuming isotropic emission, and taking into account the geometry of the experiment and the quantum efficiency of the PM tube. Assuming the probability for oxygen chemisorption on the initially clean surface to be of order 1 we arrive at $S \sim 10^{-7}$.

One would suggest that the decay of the light intensity with increasing oxygen exposure reflects a decreasing chemisorption rate. (One important property of chemiluminescence is its capability for yielding reaction rates.[1]) Let us assume that the number of photons emitted during an oxygen exposure Q is proportional to the number of chemisorbed oxygen molecules $n(Q)$, i.e.,

$$n(Q) \propto \int_0^Q I(Q)\,dQ.$$

The integral can be evaluated numerically from the I-Q curve; but to obtain an absolute scale, $n(Q)$ must be known for some Q. It has been suggested from vacuum microbalance measurements that one physical monolayer ($N = 1.13\times10^{15}$ atoms/cm^2) is adsorbed at an oxygen exposure of $Q \approx 10^{-4}$ Torr sec.[4,5] Matching to this value we obtain the number of physical monolayers $n(Q)/N$ given above the Q axis in Fig. 1. The change in slope at $Q \approx 10^{-4}$ may be due to a monolayer formation as pointed out in Refs. 4 and 5.

The slope of the I-Q curve at 10^{-2}–10^{-1} Torr sec is -1.1, which agrees with the expected slope -1 for the reported direct logarithmic law.[6] If the I-Q curve is extrapolated with a slope -1.1, an asymptotic value of $N(Q)/N \approx 4.5$ is obtained for large Q, corresponding to an Al_2O_3 thickness of ≈ 10 Å.

The considerations above support the assumption that $I(Q)$ is proportional to the chemisorption rate. There are, however, several factors which can cause a deviation from a simple proportionality: (i) S may change with increasing exposure. (ii) The spectral distribution may change with exposure (since the sensitivity of the PM tube is wavelength dependent). (iii) If there is simultaneously more than one adsorption mechanism, each will probably be measured with a different weight because of (i) and (ii). For instance, physical adsorption will not be detected at all. (iv) The I-Q curves may, especially at large exposures, be affected by the actual pressure used to obtain a given exposure (e.g., when diffusion is rate determining).

I-Q curves for Mg + O_2 have the same general form as the Al + O_2 curves, but the intensity decrease is somewhat slower at larger exposures. They also contain fine structure which, as shown below, is partly due to (ii).

An obvious extension of the investigation was to explore the spectral distribution of the emitted light. The small light intensities and the dynamics made these experiments much more elaborate. Dispersion was obtained with a 0.25-m blazed grating monochromator. The investigated wavelength regions were 3000–6500 and 3000–8000 Å for Al and Mg, respectively. Resolution had to be kept as low as 400 Å to save intensity. Two techniques were used: synchronous detection of chopped light, and photon counting. The former required fairly large pressures ($>10^{-6}$ Torr) and slow wavelength scans, which severely influenced peak shapes, peak positions, and relative intensities. One such spectrum from the Al + O_2 reaction is shown in Fig. 2. The arrow indicates the sweep direction. With opposite sweep direction only the short-wavelength peak was observed. Thus it is only relevant to discuss the gross structure of these spectra. From several runs it was concluded that the spectrum consists of a broad band from 4600 Å to at least 6200 Å with maxima at about 5100 and 5900 Å (after correction for the PM-tube sensitivity). The uncertainty in peak positions is about 200 Å. A separate test of emission in the uv region 1800–

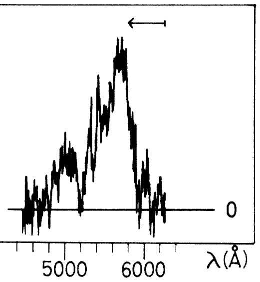

FIG. 2. Spectral distribution of the light emitted during the Al + O_2 reaction. Arrow indicates sweep direction.

3000 Å gave no detectable signal.

Most spectra from Mg + O_2 were taken with the pulse-counting technique. This permitted the wavelength region of interest to be scanned in 10 sec, and the data from each scan were added in a multichannel analyzer. The spectra from Mg + O_2 showed a definite wavelength shift with increasing oxygen exposure. The spectral distributions of the photons emitted in the exposure regions 0–10^{-4} and 10^{-4}–10^{-1} Torr sec are shown in Figs. 3(a) and 3(b), respectively. The number of counts in each channel of the memory unit was only about 50 and the number of dark counts about 5. With the synchronous detection technique the spectrum in Fig. 3(c) was obtained in the low-exposure region. The peak position is in agreement with that in Fig. 3(a), but the dynamical intensity change strongly affects the peak shape in this case. With a red-sensitive PM tube (EMI 9659) little change was observed for the small-exposure region, but the peak in Fig. 3(b) was found to extend to at least 7500 Å. The conclusion about the Mg + O_2 spectra is that one peak develops at about 4700 Å (2.6 eV) during the initial oxygen adsorption, and that most of the light for larger exposures is emitted over a wide wavelength region with a maximum at 5600 Å (2.2 eV). (The peak positions are corrected for the spectral response of the PM tube.) The wavelength shift with increasing oxygen exposure was also verified by using optical cutoff filters during the recording of I-Q curves.

The amount of experimental data is insufficient to allow a decisive conclusion about the mechanism responsible for the light emission. The energy source is of course the binding energy of oxygen to the metal, which is released in phonon excitations (heat) except in rare cases. Generally, an oxygen molecule on a metal surface initially constitutes an excited state of the system, which eventually makes a transition to a state of lower energy. The transition may with a small probability cause photon emission. This process would be analogous to molecule formation by atom recombination, a process which is radiative with a probability of $<10^{-5}$ per collision.[7] Another mechanism could be the release of excited molecules from the surface.

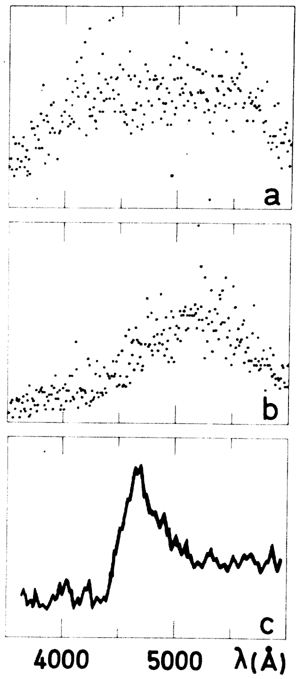

FIG. 3. Spectral distribution of the light emitted during the Mg + O_2 reaction: (a) Low-exposure region, $Q < 10^{-4}$ Torr sec. (b) High-exposure region, $Q > 10^{-4}$ Torr sec. (c) Same as (a) with synchronous detection at 5×10^{-6} Torr.

On the basis of the presented results and recent similar studies of the Na + Cl_2[8] system, I believe that valuable information about the chemisorption kinetics and bonding can be obtained by the described method.

The author wishes to thank S. Andersson for valuable suggestions and fruitful discussions throughout this work, U. Jostell for valuable experimental assistance, and H. Hammarqvist for good electronic work. Financial support from The Swedish Natural Research Council and the Swedish Board for Technical Development is also gratefully acknowledged.

---

[1] R. F. Vassil'ev, in *Progress in Reaction Kinetics*, edited by G. Porter (Pergamon, London, 1967), Vol. 4,

p. 305.

[2] B. McCarrol, J. Chem. Phys. 50, 4758 (1969).

[3] L. E. Brus and J. Comas, J. Chem. Phys. 54, 2771 (1971).

[4] E. E. Huber, Jr., and C. T. Kirk, Jr., Surface Sci. 5, 447 (1966).

[5] Wm. H. Kreuger and S. R. Pollack, Surface Sci. 30, 263 (1972).

[6] E. E. Huber, Jr., and C. T. Kirk, Jr., Surface Sci. 9, 217 (1968).

[7] G. Herzberg, *Molecular Spectra and Molecular Structure: I. Spectra of Diatomic Molecules* (Van Nostrand, Princeton, N. J., 1950), 2nd ed. pp. 400–405.

[8] B. Kasemo and L. Wallden, to be published.

Evidence for the Role of Conduction Electrons in the Kapitza Resistance*

F. Wagner,† F. J. Kollarits,‡ and M. Yaqub
Department of Physics, The Ohio State University, Columbus, Ohio 43210

(Received 11 February 1974)

Measurements of the Kapitza conductance by the ac technique between 1.2 and 1.8 K are reported for thin oriented single-crystal disks of high-purity gallium. The data show convincing evidence that the conduction electrons play a dominant role in the transmission of heat across the metal–He-II interfaces.

Theoretical investigations of Kapitza conductance $h_{\rm K}$ between metals and liquid He are invariably treated on the basis of the Khalatnikov[1] model, which explains the resistance in terms of the acoustic transmission and reflection of thermal phonons and, above 1 K, obtains numerical values 10 to 50 times smaller than those observed experimentally. In an attempt to remove the disagreement, Little[2] suggested that the electrons in a metal interact with the surface phonons to provide an additional mechanism for heat transfer. Although their calculations of this mechanism did not alter the disagreement appreciably, Little[3] and Andreev[4] independently showed that in a free-electron metal the electronic contribution to $h_{\rm K}$ is comparable to that of the phonons. At the same time Little[3] pointed out that the calculations are based on several simplifying assumptions and therefore cannot agree quantitatively with real metals, in which band-structure effects can alter absolute magnitudes considerably. Nevertheless, experiments should be able to verify the calculations by measuring the change in $h_{\rm K}$ when a metal is magnetized from the superconducting to the normal state. Well below the transition temperature, electrons take no part in heat flow and a reduction in $h_{\rm K}$ should occur. The largest change is predicted for Pb, which has been studied by several investigators[5] who have found $h_{{\rm K}n}/h_{{\rm K}s}$ to vary from 1.3 to 15. Hg, In, and Sn in general gave smaller ratios but these also differed from one experiment to another.[5] Originally this was considered evidence for the electronic contribution. Subsequent work by Cheeke,[6] however, has shown that strain at the metal surface can result in spuriously large values for $h_{{\rm K}n}/h_{{\rm K}s}$ and that the differences in the two states are mainly due to this rather than to real differences in the transmission coefficient.

In his calculations Little[3] also shows that the electronic contribution to $h_{\rm K}$ comes from two different mechanisms. In one of these the electronic coupling with the surface waves is very sensitive to the curvature of the electron orbits and their angle of incidence at the surface. Thus $h_{\rm K}$ should alter in a magnetic field H applied parallel to the metal surface. Attempts to observe this in Pb, Hg, and Cu have proved inconclusive.[5] From all these results, the generally accepted conclusion[7] is that the electrons, in spite of being the main carriers of heat in the bulk, are unable to absorb energy directly from the helium phonons striking the metal surface. It is for this reason that the problem is always treated on the basis of phonon transmission for both metals and dielectrics. In this paper we show that the above conclusions are not of general validity and that under favorable conditions electrons can indeed play a dominant role in the transfer of heat across the surface.

We have measured $h_{\rm K}$ of oriented single-crystal disks of gallium between 1.2 and 1.8 K by an improved version of an ac technique first sucessfully used by Challis and Sherlock[8] for polycrystalline metal foils. It determines the coupling between two second-sound resonating cavities separated by a thin metal foil whose thickness $l \ll \kappa/h_{\rm K}$, where κ is the bulk thermal conductivity.