Resonance-Enhanced Vibrational Excitation in Electron Scattering from O_2 Multilayer Films

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Electron-impact intramolecular vibrational and vibronic excitation of disordered multilayer O_2 films is studied with primary energies varying from 2 to 20 eV. The intensity of the $v = 1$ to $v = 4$ vibrational modes of ground state O_2 exhibits a broad resonance as a function of electron energy. At the resonance maximum the vibrational intensities are enhanced by one to two orders of magnitude. The resonance appears to be derived from gas-phase O_2 quasibound states.

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Electron scattering from molecules in gaseous and condensed phases at low energies (0–30 eV) may be divided into two broad categories, namely into resonant and nonresonant processes.[1,2] Resonance scattering is well documented in gases, where the presence of transient negative-ion states can enhance inelastic cross sections by orders of magnitude and often govern inelastic processes.[3] In condensed systems, resonance scattering has been inferred from multiple-scattering calculations for oriented molecules performed by Davenport, Ho, and Schrieffer.[4] Experimental evidence, however, is not conclusive. Ho *et al.*[5] find that the intensities of several vibrational modes of hydrogen on W(100), plus an overtone, exhibit a "resonantlike" behavior as a function of impact energy. They conclude that energy-dependent fluctuations in vibrational intensities mainly reflect changes in the reflectivity of the metal surface, including features due to beam threshold effects and surface-state resonances.[5] Tong, Li, and Mills[6] arrive at a similar conclusion from calculations of electron scattering produced by vibrations of an overlayer of CO on Ni(100). They suggest that the inner potential of the metal removes the gas-phase 1.7-eV resonance.

In the present experiment, monochromatic electrons scattered from *multilayer* (~ 50 Å) *disordered* molecular oxygen films are energy analyzed and studied as a function of primary beam energy. Since most interactions occur within the first few layers of the film, the metal substrate on which oxygen molecules are deposited is not expected to influence appreciably the scattering mechanism. Also, because of disorder in the film, its reflectivity should be largely determined by molecular potential scattering with minimal coherent enhancement of the outgoing electron wave function. Under these conditions, we show that the production of intramolecular vibrational excitation in condensed O_2 is increased by orders of magnitude by the presence of a broad electron resonance in the range 4–14 eV.

The apparatus consists of a pair of concentric hemispherical electrostatic deflectors and a closed-cycle refrigerated cryostat.[7] Both components are housed in a UHV system. The electron beam leaving the monochromator is incident on a clean polycrystalline niobium ribbon secured by a press fit to the cold end of the cryostat. The angle of incidence can be varied from 14° to 70° from the normal. Condensed layers of molecular oxygen are grown on the ribbon and thicknesses estimated, within 50% accuracy, from gas kinetic theory and work-function-change measurements, as previously described.[8] Electrons reflected at 45° from the film enter the analyzer. The entrance optics of the analyzer and exit optics of the monochromator consist of two programmable "zoom" lenses. With this configuration, it is possible to keep constant focus over wide energy limits (e.g., 2–20 eV). The resolution is 15 meV, the primary current 5×10^{-10} A, and the cold head temperature 14 K.

The energy-loss spectra for electrons of 9, 20, and 3 eV incident at 45° on a 50-Å O_2 film are represented in Fig. 1 by the upper, middle, and bottom curves, respectively. The vertical gain for each curve (×100) or portion of a curve (×20 and ×200) is referenced to the elastic peak of the top tracing. The first vibrational progression, extending from 0 to 1.5 eV in the top curve, exhibits an *average* anharmonicity of 2.8 ± 0.3 meV that is typical of vibrational excitation of ground-state $X\,{}^3\Sigma_g{}^-$ molecular oxygen (i.e., 2.75 meV calculated from the first eight levels[9]). The first five vibrational levels have energies of 195, 385, 573, 758, and 938 ± 4 meV which compare with the values of 194, 386, 575, 760, and 943 meV for

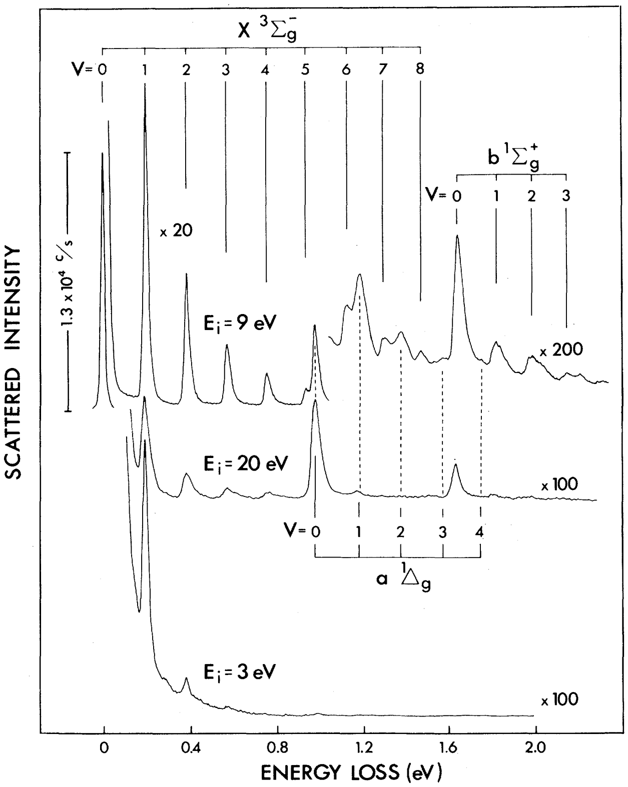

FIG. 1. Electron energy-loss spectra of a multilayer disordered O_2 film (~ 50 Å) recorded at primary energies of 9, 20, and 3 eV. The intensity of the elastic peak is indicated in counts/second (c/s).

the corresponding vibrational states measured in gaseous O_2 by optical methods.[9] From these observations and the intensity relationship between the elastic peak and each vibrational level, we conclude that these modes are not due to multiple inelastic collisions but are *overtones* of the fundamental vibration of the ground state of O_2. Other energy-loss peaks in the top curve can be ascribed to electronic and vibronic transitions belonging to the gas-phase configurations $a^1\Delta_g$ and $b\,^1\Sigma_g^+$. As in the case of the $X\,^3\Sigma_g^-$ state, their vibrational spacings were measured to an accuracy of ± 4 meV, by use of extended energy scales, and found to be the same as those of the free molecule.[9] The remaining curves in Fig. 1 indicate that all vibrational and vibronic transitions are much less intense at impact energies of 3 and 20 eV. Peak intensities are compared in Table I. Each level is normalized to its value at 9 eV taken to be unity. With the exception of the first mode, vibrational levels are enhanced by a factor of 25 to 100 at 9 eV. Furthermore, at this energy, the intensities of levels 1 to 4 represent, respectively, 6.4%, 2.7%, 1.3%, and 0.7% of the elastic current scattered into the analyzer. Similar results have been obtained with gaseous O_2 by Wong, Boness, and Schulz.[10] Their experimental points for the energy dependence of vibrational excitation of the first mode of the state $X\,^3\Sigma_g^-$ are shown at the bottom of Fig. 2. The top curve represents the reflectivity of the O_2 film. The others give the energy dependence of vibrationally excited ($X\,^3\Sigma_g^-$, v = 1 to 4) and electronically excited ($a\,^1\Delta_g$, v = 0) molecular oxygen. As suggested by Tong, Li, and Mills,[6] these curves are not normalized to the elastic peak. They rep-

TABLE I. Relative intensities of energy-loss peaks in O_2 films.

State	Impact energy (eV)		
	9	20	3
$X\,^3\Sigma_g^-$, $v = 1$	1.0	0.05	0.12
$X\,^3\Sigma_g^-$, $v = 2$	1.0	0.04	0.02
$X\,^3\Sigma_g^-$, $v = 3$	1.0	0.03	0.01
$X\,^3\Sigma_g^-$, $v = 4$	1.0	0.03	⋯
$a\,^1\Delta_g$, $v = 0$	1.0	0.25	⋯

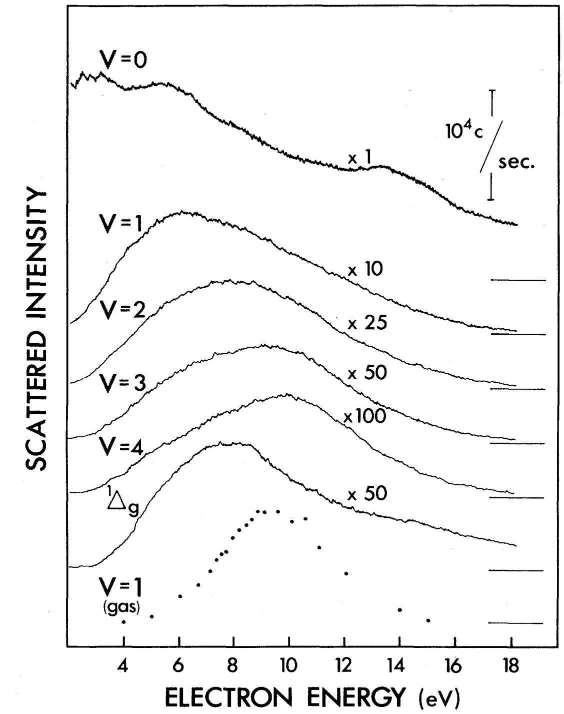

FIG. 2. Energy dependence of the reflectivity (top curve) and of vibrational and electronic excitation processes in a multilayer O_2 film. Each excitation function exhibits a broad resonance similar to that observed in gaseous molecular oxygen (bottom curve).

resent direct recordings of each energy-loss process with vertical gains referenced to the top tracing. The zero-intensity base line is indicated on the right-hand side of each curve. The energy scale has been determined by measurement of the onset of current transmitted through the film and is believed to be accurate within ± 0.3 eV.

All energy-loss processes at the solid surface show a resonance similar to that observed by Wong, Boness, and Schulz[10] in gaseous O_2. Other sharper features observed by Sanche and Schulz[11] in the total scattering cross section from 8 to 13 eV are not present in our spectra. The line shapes of the energy-loss curves in Fig. 2 are uncorrelated to the film reflectivity. This was verified by changing the elastic reflection coefficient in varying the incidence angle with respect to the normal of the film surface. However, in experiments where we produced strong oscillations in the reflectivity by covering the film with approximately a monolayer of argon, we noticed structures in the energy-loss functions that could be correlated to undulations in the reflectivity. Normalizing inelastic currents to the elastic peak also introduced extraneous features. Thus, it appears desirable to keep the reflectivity curve as smooth as possible in order to observe molecular scattering effects. Whereas in the gas phase, the energy of the resonance does not vary with the vibrational exit channel, the resonance maximum in the solid shifts from 6.0 eV ($v=1$) to 9.8 eV ($v=4$) with increasing vibrational quantum number. Such a 3.8-eV shift cannot be attributed to the slight change in reflectivity which occurs when the electron loses energy to vibrational excitation since it is much larger than the energy loss (e.g., 0.8 eV for $v=4$). Furthermore, the $a\,^1\Delta_g$ channel has a resonance maximum much less shifted in energy than that of the $v=4$ channel which lies at about the same energy (i.e., both states produce energy-loss electrons having about the same reflectivity).

A priori, vibrational excitation by electron impact of ground-state molecules can be induced via three mechanisms: through collisional momentum transfer, the dependence on internuclear separation of the interaction potential, and the formation of a shape resonance (i.e., an anion state consisting of a ground-state molecule plus an electron temporarily captured in a usually unfilled orbital). The first process is inefficient because of the small electron-to-molecule mass ratio. The second process can produce strong intramolecular vibrational excitation when the target molecule possesses a permanent dipole moment.[12] The oxygen molecule has no dipole moment, but on a metal surface its valence orbitals can be severely distorted so as to induce a permanent dipole moment.[13] However, as a result of selection rules[2] the dipolar coupling of the incident electron to the adsorbate vibrations is not an efficient mechanism for producing *overtones* of the fundamental frequency. The third mechanism is known[10] to be effective to produce, in gaseous O_2, a large increase in vibrational excitation which is of the *same order of magnitude* as that observed in the present work. We therefore suggest that the observed enhancement of vibrational and electronic excitation results from the formation of a *temporary negatively charged state (or states) of the solid* closely related to gas-phase excited states of O_2^-.

Wong, Boness, and Schulz[10] find that the anion state $^4\Sigma_u^-$ is predominantly responsible for the maximum near 9.5 eV in the vibrational excitation cross sections, but attribute the excitation of the state $a\,^1\Delta_g$ primarily to the $^2\Pi_u$ configuration of O_2^-. The states $^2\Pi_u$ and $^4\Sigma_u^-$ intercept the Franck-Condon region within the range 6–8 and 8–12 eV,[14] respectively, where we observed the largest enhancement of vibrational excitation. Both of these states can decay into ground state O_2. It is therefore possible that the energy shift, observed in the resonance maximum from the $v=1$ to the $v=4$ mode, arises from an admixture of the $^2\Pi_u$ and $^4\Sigma_u^-$ anion states whose relative contribution would vary according to decay channel. We also note that such a displacement toward higher energies is predicted from shape resonance theory,[15] when the lifetime of the resonance is short compared to a vibrational period of the molecule (i.e., in the impulse limit). From the width of the resonance we find that the impulse limit is applicable to our results but we do not know if resonances near the surface of a solid can be directly interpreted in terms of purely molecular-orbital configurations. The electron-molecule potential responsible for the formation of a shape resonance[3] is expected to be modified in condensed phases by the presence of neighboring polarizable molecules. Further theoretical and experimental work is therefore needed to evaluate the magnitude of this perturbation and to determine more precisely the nature of the electron-solid interaction.

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Quasielastic Light Scattering from Superionic PbF_2

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We have measured the intensity autocorrelation of light scattered from PbF_2 in the temperature range 110 to 524 °C. The observed relaxation times are too long to be caused by F^- diffusion. Alternative mechanisms are considered, including the diffusion of Pb^{++} or neutral lead. This is the first measurement of fluctuations in a superionic conductor by photon correlation spectroscopy.

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Superionic conductors achieve conductivities normally characteristic of the melt at temperatures below the melting point. In PbF_2 the conductivity continuously rises to saturation and the specific heat exhibits an anomalous peak well below the melting point. These and other characteristics suggest a large population of lattice defects. In PbF_2 the fluorine-ion defect concentration and mobility increase dramatically below the melting point. The properties of superionic conductors have been reviewed by Boyce and Huberman[1] and Salamon.[2]

Raman and Brillouin light scattering in superionic conductors clearly give evidence of anharmonicity and disorder associated with the high conductivity.[3,4] In addition to broad propagating modes, there are strong, quasielastic peaks attributed to hydrodynamic modes. In two cases,[5,6] the measured widths of the Lorentzian peaks (0.3 and 3.8 cm^{-1} for $RbAg_4I_5$ and α-AgI, respectively) are consistent with relaxation rates estimated from the diffusivity of the mobile ion. In addition, narrower Rayleigh peaks have been observed in these quasielastic measurements in the frequency domain.

Quasielastic light scattering in the time domain is a well established technique for the measurement of the diffusivity of particles in liquids.[7] The coherent scattered E field due to suspended submicron-sized particles, undergoing Brownian motion, will fluctuate as the particles diffuse over distances comparable to $\lambda/2$. These interference fluctuations will cause the intensity autocorrelation function to relax with a characteristic time τ, such that

$$\tau = (DK^2)^{-1}, \tag{1a}$$

where K is the scattering wave number,

$$K = 4\pi n \lambda^{-1} \sin(\theta/2), \tag{1b}$$

and D is the particle diffusivity. In Eq. (1a) we have assumed a heterodyne experiment where the scattered E field which is random in time beats against a stationary local oscillator.

The situation in a solid is similar. In an imperfect crystal a nonuniform distribution of defects will cause elastic light scattering. Adam, Searby, and Bergé[8] have measured the intensity