

Search for the plasmon in condensed water

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Creation of plasmons in water by energetic particles in biological tissue is important because this form of energy can migrate from the place of excitation and be transferred to nearby molecules like DNA. We have searched for evidence of plasmons in solid water, using electron-energy-loss and secondary electron spectroscopies excited by 70–1000-eV electrons. We find that the energy of the main excitation, often attributed to plasmons, depends on the energy of the exciting electron, unlike the expected plasmon behavior. The energy spectrum of secondary electrons shows the presence of autoionization, but no evidence of plasmon decay.

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Electronic excitation in water by ionizing radiation may cause dissociation when it is converted into molecular motion through repulsive interactions. This type of radiation damage can have consequences ranging from the stability of biological systems to the erosion of icy planetary satellites and rings, comets, and interstellar grains. Complex calculations in radiation biology and dosimetry^{1–3} require as input the spectra of electronic excitations and the energy distributions of electrons from ionization events. In spite of decades of studies of optical-absorption and electron-energy-loss spectroscopy of condensed water, the interpretation of the findings in terms of energy levels and individual physical processes remains controversial. For instance, the most likely energy absorption in condensed water, which occurs at ~ 21 eV, was first proposed to be due to plasmons⁴ based on an estimate by Platzman.⁵ This interpretation was questioned by Daniels,⁶ based on measurements of energy-loss spectra for high-energy electrons in liquid water. Nevertheless, the plasmon idea continued to be developed theoretically,^{7,8} and was thought to be confirmed by optical reflectivity measurements by Heller *et al.*,⁹ who claimed that essentially all the energy deposited by ionizing radiation in water eventually goes into the excitation of collective oscillations at 21 eV. More recently, some authors questioned the plasmon interpretation,^{10,11} while others argued in favor of these delocalized collective excitations,^{12–14} and used the plasmon concept to estimate electron energy spectra.¹⁵ Recent inelastic x-ray scattering spectroscopy studies¹⁶ were not able to draw any conclusions as to the existence of plasmons in liquid water.

Whether ~ 20 -eV excitation in water is a plasmon or not is important because, at excitation and during their lifetime, plasmons are delocalized outside the particle track, and may affect nearby molecules when they decay. For example, DNA in biological cells could be destroyed not only by a direct hit from an ionizing particle, but by a plasmon produced in the adjacent water; the importance of the latter effect depends on the spread of the plasmon during its lifetime, and where it decays. We attempt to resolve the controversy over the existence of plasmons by using electron-energy-loss spectroscopy (EELS) and secondary electron spectroscopy on amorphous solid water. This solid is a structural analog to liquid water, and has a nearly identical electronic excitation spectrum.¹⁷ The primary electron energy range, 70–1000 eV,

differs from that typically used in transmission electron microscopy,¹⁸ and from the very low energies (< 19 eV) used to study excitation of lattice vibrations¹⁹ and excitons.²⁰ The use of EELS in our energy range to study solids was reviewed recently.²¹

The experiments were done in an ultrahigh-vacuum system. Ice was grown by passing pure H₂O vapor through a capillary array onto a Mo substrate cooled by liquid nitrogen, under conditions known to lead to the growth of the amorphous phase.²² Crystallization by annealing to the cubic phase did not produce significantly different spectra, in agreement with the report that high-energy EELS spectra are insensitive to the phase of ice.¹⁸ Electrons were incident at 40° to the surface normal. Backscattered and secondary electrons emitted with an angle of $137^\circ \pm 2^\circ$ in a cone around the incident beam were energy analyzed by a double-pass cylindrical mirror electrostatic spectrometer. The spectrometer was operated at constant pass energy of 50 eV, with a resolution of 0.2 eV independent of electron energy, and smaller than the ≈ 1 -eV energy width of the primary electron beam. The transmission function of the spectrometer was measured and used to correct the electron energy distributions to obtain $N(E)$, the intensity of scattered and secondary electrons per unit energy interval.

Figure 1 shows an energy-loss spectrum taken at 1 keV, compared to a photoabsorption spectrum.²³ Common features are transitions from the valence $1b_1$, $3a_1$, and $1b_2$ levels to the $3s4a_1$ orbital, at 8.7, 10.4, and 14.5 eV, respectively.²⁴ These energies are blueshifted by ~ 1.2 eV from the values for the free molecule,²⁵ due to the repulsive interaction of the $3s4a_1$ Rydberg orbital with surrounding molecules.²⁶ The equivalent excitation from the state $2a_1$ is expected to be at ~ 28 eV. In contrast to these excitations, the energy difference between the main peaks in the electron- and photon-excited spectra is larger and, as will be seen later, not fixed. To understand commonalities and differences we recall that the energy loss function in the EELS spectrum is proportional to $\text{Im}(-1/\epsilon) = \epsilon_2/(\epsilon_1^2 + \epsilon_2^2)$, where $\epsilon = \epsilon_1 + i\epsilon_2$ is the complex dielectric constant.²⁷ This correspondence of energy loss and $\text{Im}(-1/\epsilon)$ is strictly valid at high impact velocities, in the domain of the first Born approximation. In contrast, the optical absorbance is proportional to ϵ_2 . The common structure in both spectra of Fig. 1 results where ϵ_2 has a peak and ϵ_1 varies slowly (top panel

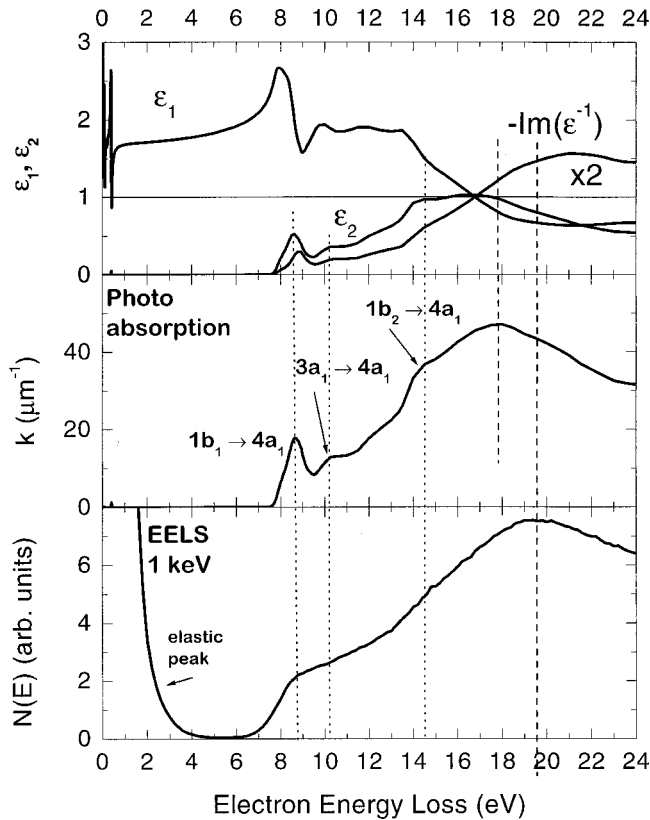


FIG. 1. Bottom panel: electron-energy-loss spectrum of water ice at 90 K for 1-eV electrons. Middle panel: optical-absorption spectrum of water ice. Top panel: real (ϵ_1) and imaginary (ϵ_2) components of the dielectric constant, and the loss function $-\text{Im}(\epsilon^{-1})$ multiplied by 2. Optical data in the top two panels are from Ref. 23.

of Fig. 1). Differences between photon and electron excitation are due to several factors. First, photons excite almost exclusively dipolar excitations with their transverse electric field. Fast electrons can produce the same transverse dipole excitations accessible with photons, and also create a wake of longitudinal excitations like plasmons. Differences in the shape of the common absorption structure may be due to the fact that low-energy (<1 keV) electrons can also produce singlet-triplet transitions through exchange with target electrons. Broadening of the spectra will result, because exchange and nonexchange transitions have close but different energies, and result from momentum transfer not possible with photons. In addition, the depth of excitation by low-energy electrons is shallow compared with that of photons, causing a larger probability of producing surface excitations, which may be different from those in the bulk.

The “plasmon peak” results when the dielectric constant becomes zero or, more loosely, when $\epsilon_1 \ll 1$. This corresponds to low screening, and therefore to a large penetration of the electric field, needed for collective excitations. In addition, the concept of plasmon oscillation is only meaningful if the oscillation lasts at least one period. This requires that $\epsilon_2 \ll 1$. Although the dielectric constant of water in this range is $\epsilon_1 \approx \epsilon_2 \approx 0.6$, so the strict conditions for plasmon formation are not really met, both the significant difference be-

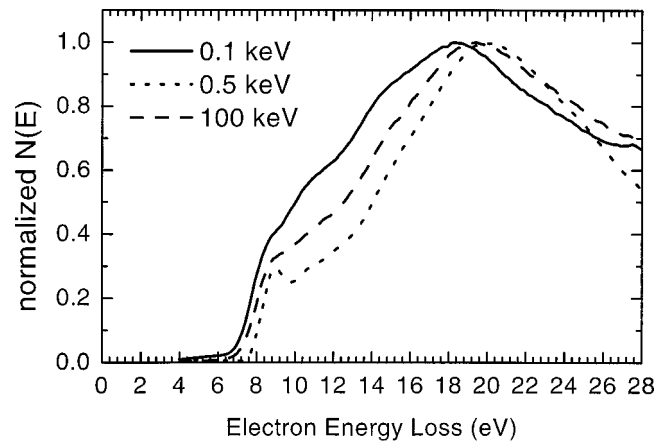


FIG. 2. EELS spectrum of amorphous ice at 100 and 500 eV, compared with 100-keV data from Ref. 31. The intensity of each spectrum is normalized so that the height of the main energy-loss peak is 1.

tween electron and photon excitation and the broadness of the structure at ~ 21 eV could be taken as indication of a “frustrated plasmon,” a coherent collective excitation that decays before completing an oscillation.

A further test of the plasmon hypothesis is obtained by varying the electron impact energy. A recent theoretical study²⁸ predicted that the shapes of the excitation spectra at 100 and 500 eV should be very different, but that the peak energies should be the same. This is not confirmed by our experiments (Fig. 2), which show that the shape changes very little, although the peak energy is seen to shift slightly to high values. This shift in peak energy with impact energy is an important finding, since the energy of an elementary excitation like a plasmon should not be affected by the excitation conditions, except for a small increase with momentum transfer q (dispersion).²⁹ For bulk plasmon excitations, dispersion produces an increase of plasmon energy when the energy of the projectile is *decreased* and a larger q is needed for the same energy transfer. This behavior is opposite to that shown in Fig. 3, which plots the position of the main energy-loss peak as a function of electron energy, together with previous results.^{6,30,31} A possible reason for the shift of peak energy with impact energy is that several states contribute to the peak, each having different excitation probability as a function of electron energy. A candidate is the excited ionic $\text{H}_2\text{O}^+(B)$ state,³² giving a photoabsorption peak at around 17.8 eV in the gas phase, and which should be blue-shifted to about 19 eV in the solid. Other likely channels are double-electron excitations,³³ which are more likely excited by electrons than by photons.

The observation of secondary electrons provides a second tool to search for the plasmons, since the preferred decay mode of these excitations is the formation of an electron-ion pair in an interband transition.²⁷ A ~ 21 -eV plasmon should produce an excitation spectrum resembling that of ultraviolet photoemission with the He I line (21.2 eV), or with Penning ionization by He $1s2s$.³⁴ That is, it would show the three peaks due to ionization of the $1b_1$, $3a_1$, and $1b_2$ levels, broadened by the plasmon width. This structure would be

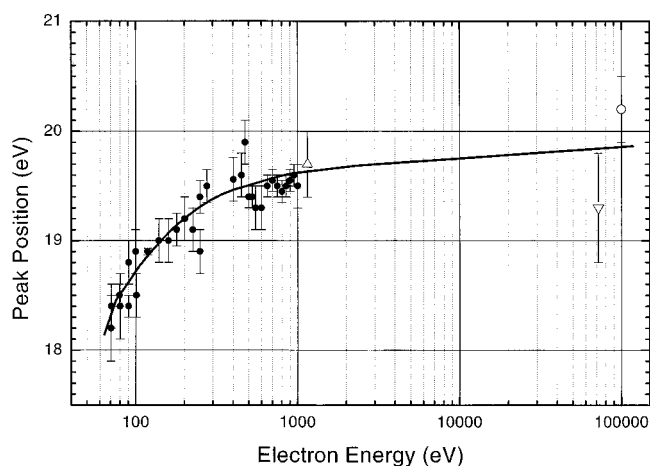


FIG. 3. Dependence of the position of the main energy loss peak on the energy of the projectile electron. Closed circles, this work; \triangle , Otto and Lynch (Ref. 30); ∇ , Daniels (Ref. 6); and \circ , Leapman and Sun (Ref. 31), taken at 1.15, 72, and 100 keV, respectively. The line is meant to guide the eye and has no other meaning.

centered at ~ 7 eV, which is the difference between the 21-eV excitation energy and the separation of ~ 14 eV between the middle of the valence band and the vacuum level. The measured spectra (Fig. 4) do not show such a structure. Rather, in addition to the typical secondary electron peak at ~ 2 eV, we find a structure peaking at ~ 11 eV, 4 eV higher than predicted for the plasmon decay.³⁵ In Fig. 4 we also show this structure more clearly, after subtracting a smooth background. We interpret those electrons to originate from the autoionization decay of the state $2a_1^{-1}4a_1$ (estimated energy ~ 28 eV; see above), resulting in a final hole in a valence level. In contrast to the case of the main peak in the EELS spectra, the peak energy of this secondary electron structure does not depend on primary electron energy, and therefore is not correlated with the energy of the main loss peak shown in Fig. 3.

In summary, different experimental evidence presented here stands against the idea of ordinary plasmons in water. The main electron-energy-loss peak does not occur at a fixed energy, as expected from an elementary excitation, but shifts to high energies as the impact velocity increases. On the other hand, the fact that this main energy loss does not coincide with a peak in photoabsorption (or ϵ_2), but occurs

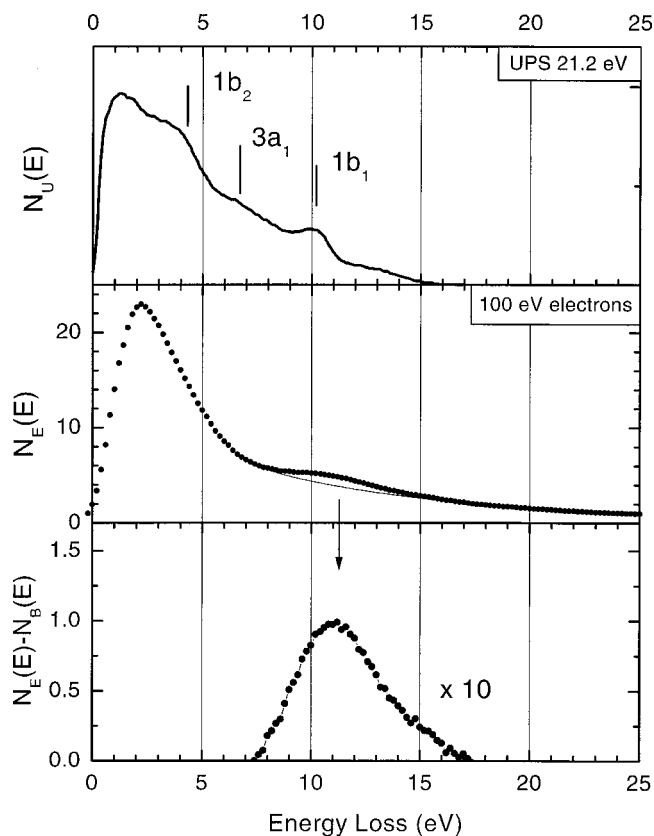


FIG. 4. Middle panel: N_E , energy spectrum of secondary electrons ejected from a water ice film by 100-eV primary electrons. Top panel: ultraviolet photoelectron spectrum N_U at 21.2 eV (Ref. 34). A similar, but broadened, structure would be expected from the decay of a 21-eV plasmon. Bottom panel: extraction of the 11-eV peak from $N(E)$ after the subtraction of the background N_B .

close to a minimum in ϵ_1 , suggests the existence of some kind of collective excitation. The spectrum of secondary electrons shows no evidence of plasmon decay. Instead, we discovered a significant decay channel, likely due to an autoionization process in the solid which might lead to radiation damage or desorption of surface molecules.³⁶ The conclusion presented here may be applicable to radiation effects in other molecular substances, including DNA, which have been thought to support delocalized plasmon excitations.³⁷

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