

Observation of Negative Ion Resonances in Amorphous Ice via Low-Energy (5–40 eV) Electron-Stimulated Production of Molecular Hydrogen

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The $D_2(^1\Sigma_g^+, v = 0-2, J = 0-2)$ desorbates produced during low-energy (5–40 eV) electron-beam irradiation of amorphous D_2O ice were monitored using resonance-enhanced laser ionization spectroscopy. We attribute the structure in the D_2 yield as a function of the incident electron energy to core-excited negative ion resonances. These resonances, or the excited states produced after electron autodetachment, decay via molecular elimination to yield $D_2(^1\Sigma_g^+)$ directly. D_2 is observed with $v = 0$ or 2 but not $v = 1$, suggesting a symmetry propensity in the excitation or decay of the resonances. [S0031-9007(96)01483-4]

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The formation of negative ion resonances during scattering of low-energy electrons with atoms, molecules, surfaces, and interfaces is a process of fundamental importance in physics, materials science, chemistry, and radiation biology. In general, electron collisions with isolated molecules can lead to a variety of negative ion resonances such as dipole-bound, single-electron shape, and multi-electron core-excited resonances [1–3]. The core-excited resonances, which are the topic of this Letter, generally consist of an excess electron temporarily bound by the positive electron affinity of an electronically excited target molecule. These resonances are generally two-electron, one-hole configurations which are classified as either Feshbach or core-excited shape resonances [1,2].

The majority of negative ion resonances decay by electron autodetachment producing vibrational and/or electronic excitation which may result in dissociation of the molecule. While the electron autodetachment lifetimes of core-excited shape resonances are typically very short ($\sim 10^{-14}$ – 10^{-15} sec), the lifetimes of Feshbach resonances are somewhat longer ($\sim 10^{-12}$ – 10^{-14} sec) [1,2]. When the electron autodetachment lifetime is comparable to a vibrational period, then dissociation into a stable anion and neutral fragment(s) may result if the resonance is dissociative in the Franck-Condon region. This process is known as dissociative electron attachment (DEA).

DEA has been extensively studied in the gas phase by measuring the anion fragment yields versus incident electron energy [1,2,4,5]. Information about the symmetries and electronic structures of gas-phase core-excited resonances has been obtained by measuring the energy and angular dependence of the excitation cross sections [6,7]. More recent DEA studies have investigated attachment to optically excited states [8,9], molecular solids [10,11], and coadsorbed systems [12]. Resonances which decay via electron autodetachment to produce excited neutral states have been observed as “intermediates” in high-resolution, electron energy loss and electron-transmission

spectroscopy both in the gas phase [2,13,14] and in the condensed phase [3,15].

In this Letter, we report detailed studies of the $D_2(^1\Sigma_g^+)$ desorbates produced during low-energy (5–40 eV) electron-beam irradiation of amorphous D_2O ice. We find evidence for negative ion resonances which decay by unimolecular dissociation to *directly* produce D_2 for incident electron energies (E_i) between ~ 8 and 16 eV and between ~ 18 and 32 eV. These negative ion resonances were not observed in previous electron stimulated desorption (ESD) studies of amorphous ice which investigated the H^- (D^-) [11], D (2S), O (3P_J), and O (1D) [16] dissociation products. The higher energy structure has not been reported, even in the gas phase. In addition, for the kinetic energy range investigated in these experiments, the D_2 product is observed with $v = 0$ or 2 but *not* $v = 1$, suggesting a symmetry effect in the excitation or decay of the resonances. These results suggest that condensed-phase negative ion resonances can be investigated via detection of the *neutral* desorbates. We expect this to be quite general since both primary decay pathways of negative ion resonances, electron autodetachment, and DEA, can lead to neutral products.

The experiments were performed in an ultrahigh vacuum ($\sim 1 \times 10^{-10}$ Torr) system equipped with a pulsed low-energy electron gun, a quadrupole mass spectrometer (QMS), an effusive gas doser, and a time-of-flight (TOF) spectrometer for laser resonance enhanced multiphoton ionization (REMPI) detection of neutral desorbates. D_2O multilayers (~ 200 Å) were grown on a platinum(111) crystal at 88 K under conditions which are known to produce amorphous ice. The ice samples were irradiated with a pulsed electron beam which has an energy spread of ~ 0.3 eV, a typical current density of $\sim 10^{14}$ (electron/cm²)/sec, and a beam spot size of ~ 1.5 mm.

We utilized (2 + 1) REMPI via the $E, F^1\Sigma_g^+$ state to detect the D_2 products in the ($X^1\Sigma_g^+$) ground electronic state [17]. The estimated detection efficiency is $\sim 10^6$ (molecules/cm³)/quantum state. All the experiments

were done in the TOF mode in which the neutral D_2 molecules produced by the pulsed electron beam are resonantly ionized by the laser beam approximately 4 mm above the sample surface. A relatively long ($\sim 20\text{--}25 \mu\text{sec}$) electron beam pulse was used which integrates a range of desorbate velocities. The ionizing laser pulse was delayed with respect to the electron beam pulse such that the D_2 molecules detected in these experiments had translational energies $\leq 0.5 \text{ eV}$.

To avoid problems associated with the accumulation of reaction products and charge in the ice layer, a new amorphous ice layer was deposited after a total electron-beam exposure of $\sim 5 \times 10^{14} e^-/\text{cm}^2$. The ESD yield was sufficiently small to preclude any secondary (above the surface) interactions. In addition, the low D-atom number density in the ice and the low D—D encounter frequency at 88 K precluded any significant contribution to the D_2 yield from $D + D$ reactions on the time scale of the measurements. Finally, D_2 resulting from the ion-molecule reaction $D^- + D_2O \rightarrow D_2 + OD^-$ is unlikely since the yield of D^- versus electron energy [11], is very different than the yield of D_2 versus energy.

Figure 1 shows the yield of $D_2(v=0, J=0)$ desorbing from amorphous ice as a function of incident electron energy. The D_2 yield, which is the average of ~ 10 individual scans of the yield versus energy, has two interesting features: a small peak at $\sim 12.5 \text{ eV}$ and a broad shoulder centered at $\sim 25 \text{ eV}$. For energies above $\sim 30 \text{ eV}$, the D_2 yield versus electron energy increases monotonically with no apparent structure for all vibrational and rotational levels investigated ($v=0\text{--}3$ and $J=0\text{--}8$). We have therefore normalized the D_2 yields at energies greater than 35 eV and compare the yields as a function of the D_2 vibrational level in Figure 2. Figure 2(a) shows the D_2 yields for $J=0$ and $v=0, 1$ and 2 for $5 \text{ eV} \leq E_i \leq 40 \text{ eV}$. The uncertainties in the data, which

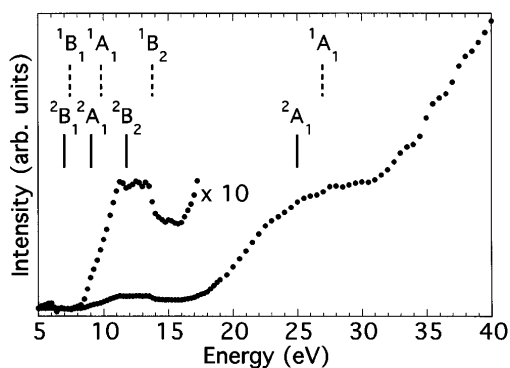


FIG. 1. $D_2(v=0; J=0)$ intensity vs electron energy. The data were acquired with the sample temperature T_s at 88 K. The D_2 intensity has a small peak at $\sim 12.5 \text{ eV}$ and a broad shoulder centered at $\sim 25 \text{ eV}$, which are due to the dissociation of core-excited negative ion resonances or the excited states produced after electron autodetachment. The energies of some excited states of the neutral molecule and the corresponding negative ion resonances, as measured in the gas phase, are indicated by the dashed and solid lines, respectively (see text).

for $v=1$ and 2 are the average of ~ 3 individual scans, can be estimated from the scatter in the data. The relative intensities of the signals at 40 eV are approximately $140:3:1$ for $v=0:1:2$. An important observation is that, for the kinetic energy range investigated in these experiments, the structure centered at $\sim 25 \text{ eV}$ in $v=0; J=0$ is also present in $v=2; J=0$, but is *weak or absent* in $v=1; J=0$. (For these data, the uncertainty is too large for $v=1$ and 2 to infer anything about the yield below $\sim 18 \text{ eV}$.) Since the overall intensity for the $v=2$ signal is weaker than the $v=1$ signal, the lack of signal between 18 and 32 eV for $v=1$ is not due to a lower detection sensitivity. A similar lack of signal intensity in the $v=1$ level relative to the $v=0$ and $v=2$ levels for $8 \text{ eV} \leq E_i \leq 16 \text{ eV}$ is shown in Fig. 2(b). The data, which are the average of ~ 10 individual scans each, were obtained via the $J=2$ transition since the signal was larger for the $J=2$ population in the $v=1$ and 2

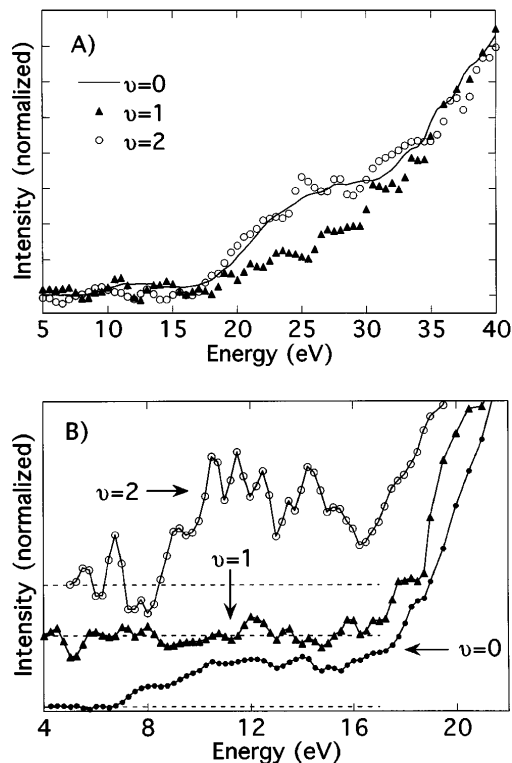


FIG. 2. Vibrational state specific intensities of D_2 vs electron energy. The curves are normalized at 40 eV . For these data, $T_s = 88 \text{ K}$ except $D_2(v=1, J=2)$ for which $T_s = 95 \text{ K}$. The observation that the state specific behavior occurs over a limited energy range suggests that negative ion resonances are responsible. (a) $D_2(v=0, 1, 2; J=0)$ intensity vs electron energy. The relative intensities of the signals at 40 eV are approximately $140:3:1$ for $v=0:1:2$. The yields of $D_2(v=0, 2; J=0)$ have a broad shoulder centered at $\sim 25 \text{ eV}$ while this feature is weak or absent for $D_2(v=1; J=0)$. (b) $D_2(v=0, 1, 2; J=2)$ intensity vs electron energy. (The curves have been offset for clarity). The yields of $D_2(v=0, 2; J=2)$ have a peak/shoulder centered at $\sim 12.5 \text{ eV}$ while this feature is weak or absent for $D_2(v=1; J=2)$.

levels. (Note that the overall lower intensity for $\nu = 2$ is reflected in the higher amount of noise in the signal.)

The structure in the D_2 yield, centered at $E_i \sim 12.5$ and ~ 25 eV in Figs. 1 and 2, suggests that negative ion resonances are primarily responsible for D_2 production at these energies. First, as discussed below, the peak in $D_2(\nu = 0, J = 0)$ yield at ~ 12.5 eV corresponds closely to a DEA resonance previously observed in the gas phase [4,5]. Second, the observation that the vibrational state specific behavior occurs only over a limited range of electron energies implies that negative ion resonances are responsible since the incident electron can be captured to form a resonance only at certain energies [1,2]. Conversely, in nonresonant electron scattering experiments, excitation of a particular electronic state can occur for a wide range of incident electron energies beyond threshold [2]. We have previously measured the ESD yields of $D(^2S)$, $O(^1D)$, and $O(^3P_J)$ from amorphous ice [16]. The $D(^2S)$ yield, which is related to the ionization cross section and electron-ion recombination, has no comparable structure in this energy range, indicating that the structure in the D_2 yield is not directly related to ionization. This is consistent with measurements of the electron impact ionization cross section in gas-phase water which show no structure in this energy range [18].

To begin the discussion of the data in Figs. 1 and 2, we briefly review the electronic structure of water. The H_2O molecule has the electronic ground state configuration $(1a_1)^2(2a_1)^2(1b_2)^2(3a_1)^2(1b_1)^2, ^1A_1$, with two empty valence shell O-H antibonding orbitals ($4a_1$) and ($2b_2$). The three lowest energy excited states (excitons), the $^3,^1B_1$, $^3,^1A_1$, and $^3,^1B_2$ are at 7.4 (~ 8.6), 9.8 (10.4), and ~ 13.8 eV (~ 14.5 eV), respectively, in water vapor (ice) [19,20]. These excited states, which are all dissociative in the gas phase, are formed by promoting an electron from one of the three highest occupied orbitals to the lowest unoccupied $3s:4a_1$ mixed Rydberg/valence orbital. They have been assigned as the "parent" configurations which give rise to the 2B_1 , 2A_1 , and 2B_2 (one-hole, two-electron) DEA Feshbach resonances [5].

As discussed in the introduction, negative ion resonances decay primarily by electron autodetachment and DEA, and both of these decay mechanisms can lead to neutral dissociation products. In the gas phase, the 2B_1 , 2A_1 , and 2B_2 DEA resonances lead primarily to H^- (D^-) and O^- [4,5,7]. The peaks in the O^- yield occur at 7.0, 9.1, and 11.8 eV, respectively [5] as indicated by the solid vertical lines in Fig. 1. In amorphous ice, previous studies have demonstrated that DEA leading to H^- (D^-) occurs via the 2B_1 and 2A_1 resonances [11]. The peak desorption for H^- (D^-), associated with the 2B_1 resonance, is at 7.4 eV. This is ~ 0.9 eV higher than the gas phase energy due to many body interactions. If we assume that the energy shift of the 2B_2 resonance is also ~ 0.9 eV, then the peak in the D_2 ($\nu = 0, J = 0$) yield at ~ 12.5 eV may correspond to the 2B_2 DEA resonance which can lead to

D_2 via $D_2O + e_{in} \rightarrow D_2(^1\Sigma_g^+) + O^-(^2P)$. The width of the feature, which has an apparent threshold at ~ 8.3 eV and extends to ~ 14.7 eV, suggests that the 2A_1 resonance also contributes to the D_2 yield.

To understand whether the negative ion resonances decay by electron autodetachment or DEA, we can consider the energies of the dissociation products. Because of the small signals involved, we were not able to measure the velocity distribution of the D_2 molecules. However, we can make some inferences about the nascent D_2 kinetic energies. First, the resonant behavior in the D_2 yield is observed for states which have vibrational and rotational excitation, e.g., $D_2(\nu = 0, J = 4)$ and $D_2(\nu = 2, J = 2)$. Second, since interactions of the D_2 molecule with the surface or bulk will quickly quench rotational excitation, these molecules most likely have not interacted with the surface and thus are representative of the nascent D_2 kinetic energy. Third, due to experimental constraints, the D_2 molecules detected in these experiments have kinetic energies ≤ 0.5 eV. Based on these considerations, we suggest that most of the D_2 molecules are formed with low kinetic energies (≤ 0.5 eV). In addition, these D_2 molecules are detected in the ground electronic state and have low internal energy ($E_{int} < 1.5$ eV). Therefore, the D_2 molecules are probably formed with less than a total energy of 2 eV. In addition, conservation of energy and momentum implies that the kinetic energy of the oxygen fragment will be small compared to that of the D_2 molecule. Since the incident electrons which initiate the dissociation have ~ 12.5 eV of energy and the minimum energy required for the reaction $D_2O + e^- \rightarrow D_2(^1\Sigma_g^+) + O^-(^2P)$ is only 3.5 eV, approximately 7 eV of energy is unaccounted for by the DEA model. These arguments suggest that the excited anions decay by electron autodetachment, either from the water anion prior to dissociation or perhaps from an electronically excited oxygen anion after dissociation. Also, electron autodetachment may result in electronically excited oxygen atoms such as $O(^1S)$.

The 2A_1 and 2B_2 autodetachment lifetimes have been calculated to be 6.0×10^{-14} and 0.8×10^{-14} sec, respectively, using *ab initio* configuration interaction techniques by Jungen *et al.* [5]. These lifetimes may be even shorter in the condensed phase due to many body interactions and the repulsion associated with the excited $3s:4a_1$ parent configuration. In particular, for higher energy negative ion resonances, coupling to the conduction band in the ice may enhance electron autodetachment. Although we believe that the 2A_1 and 2B_2 resonances are the initial excitations leading to D_2 at ~ 12.5 eV, we note that other negative ion resonances may be responsible. For example, in this energy range, several negative ion "compound" states have been observed in gas-phase electron transmission studies [21].

Most previous studies of negative ion resonances in gas-phase water have primarily investigated processes at

electron energies below ~ 20 eV. However, it is likely that electronically excited states formed by promoting an electron from the $2a_1$ orbital to low lying unoccupied orbitals such as the $3s:4a_1$ will also have a corresponding negative ion resonance. For example, using a Rydberg term value of ~ 5 eV [19] places the 3,1A_1 ($2a_1 \rightarrow 3s:4a_1$) at ~ 27 eV and the corresponding 2A_1 resonance at ~ 25 eV, as indicated by vertical lines in Fig. 1. We would expect a core-excited resonance associated with an excitation from the $2a_1$ orbital to dissociate, and we suggest that this resonance, and the satellites associated with decay of this deep valence level [22], are responsible for the structure between 18 eV and 32 eV. Note that for this resonance, even more excess energy is available and so electron autodetachment prior to dissociation or from an excited oxygen anion after dissociation is very likely. This is consistent with a gas-phase DEA study which reports no structure in the O^- yield for $18 \text{ eV} < E_i < 30 \text{ eV}$ [23].

We offer two possible explanations for the interesting vibrational state dependence observed in the D_2 products (Fig. 2), both of which are related to the Franck-Condon overlap of the vibrational wave functions in the ground and excited electronic states. The lack of D_2 in $\nu = 1$ suggests that one vibrational mode of the D_2O core-excited resonance correlates adiabatically with the vibrational excitation in the D_2 product. For example, if the asymmetric stretch (ν_3) in the excited state correlates with the D_2 vibration, then no D_2 ($\nu = 1$) will be produced since the overlap between the initial vibrational wave function, which at 88 K will be in the ground state (symmetry A_1), and the excited state wave function is zero for states with $\nu_3 = \text{odd}$ (symmetry B_2) [24]. However, for excited states with $\nu_3 = \text{even}$, the symmetry is A_1 and the Franck-Condon overlap can be nonzero. Another possibility is that the symmetric stretch (ν_1) in the D_2O excited state correlates with the D_2 vibration. In that case, the overlap between the ground and excited state will not necessarily be zero since both wave functions have A_1 symmetry. However, if the "equilibrium" positions for the nuclei along the symmetric stretch coordinate in the excited state are the same as in the ground state (i.e., if the O-H bond distance is the same in both states), then the Franck-Condon overlap between the initial vibrational wave function and odd vibrational levels in the electronically excited state will be small or zero, again leading to an absence of D_2 ($\nu = 1$). To distinguish between these and other possible explanations for the behavior seen in Fig. 2, it would be useful to have realistic calculations of the potential energy surfaces in this energy range.

In summary, we report evidence for negative ion resonances produced during low-energy (5–40 eV) electron-beam irradiation of amorphous ice. These resonances, or the excited states produced after electron autodetachment, dissociate to yield $D_2(^1\Sigma_g^+)$ directly. D_2 is observed with

$\nu = 0$ or 2 but not $\nu = 1$ indicating a symmetry effect in the excitation or decay of the resonances. This is the first study to demonstrate the existence of condensed-phase negative ion resonances via the detection of neutral desorption products.

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- [1] *Electron-Molecule Interactions and Their Applications*, edited by L.G. Christophorou (Academic, New York, 1984), Vol. 1.
- [2] *Electron-Molecule Collisions*, edited by I. Shimamura and K. Takayanagi (Plenum Press, New York, 1984).
- [3] R. Palmer and P.J. Rous, *Rev. Mod. Phys.* **64**, 383 (1992).
- [4] R.N. Compton and L.G. Christophorou, *Phys. Rev.* **154**, 110 (1967).
- [5] M. Jungen, J. Vogt, and V. Staemmler, *Chem. Phys.* **37**, 49 (1979).
- [6] R. Azria, Y.L. Coat, G. Lefevre, and D. Simon, *J. Phys. B* **12**, 679 (1979).
- [7] D.S. Belic, M. Landau, and R.I. Hall, *J. Phys. B* **14**, 175 (1981).
- [8] L.G. Christophorou *et al.*, *Phys. Rev. Lett.* **58**, 1316 (1987).
- [9] L. Siller *et al.*, *Phys. Rev. Lett.* **76**, 1960 (1996).
- [10] L. Sanche, *Phys. Rev. Lett.* **53**, 1638 (1984).
- [11] P. Rowntree, L. Parenteau, and L. Sanche, *J. Chem. Phys.* **94**, 8570 (1991).
- [12] L. Sanche, A.D. Bass, P. Ayotte, and I.I. Fabrikant, *Phys. Rev. Lett.* **75**, 3568 (1995).
- [13] L. Sanche and G.J. Schulz, *Phys. Rev. A* **6**, 69 (1972).
- [14] D. Cvejanovic, L. Andric, and R.I. Hall, *J. Phys. B* **26**, 2899 (1993).
- [15] M. Michaud and L. Sanche, *Phys. Rev. Lett.* **59**, 645 (1987).
- [16] G.A. Kimmel and T.M. Orlando, *Phys. Rev. Lett.* **75**, 2606 (1995).
- [17] K.-D. Rinnen *et al.*, *J. Chem. Phys.* **95**, 214 (1991).
- [18] T.D. Mark and F. Egger, *Int. J. Mass Spectrom. Ion Phys.* **20**, 89 (1976).
- [19] P. Gurtler, V. Saile, and E.E. Koch, *Chem. Phys. Lett.* **51**, 386 (1977).
- [20] K. Kobayashi, *J. Phys. Chem.* **87**, 4317 (1983).
- [21] L. Sanche and G.J. Schulz, *J. Chem. Phys.* **58**, 479 (1973).
- [22] D.E. Ramaker, *Chem. Phys.* **80**, 183 (1983).
- [23] C.E. Melton and G.A. Neece, *J. Chem. Phys.* **55**, 4665 (1971).
- [24] E.B. Wilson, J.C. Decius, and P.C. Cross, *Molecular Vibrations: The Theory of Infrared and Raman Vibrational Spectra*, (Dover Publications, New York, 1955), p. 388.