

## Atomic oxygen in solid deuterium

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Atomic oxygen is photogenerated in solid  $D_2$  by 193 nm irradiation of samples initially doped with molecular oxygen. The atoms are detected by laser-induced fluorescence at the  $O(^1S \rightarrow ^1D)$  transition, which occurs at 559 nm, with a fluorescence lifetime of 230  $\mu s$ . The absorption leading to this emission is indirect, attributed to  $O_2(X):O(^3P)$  pairs. Complementary studies are carried in solid  $D_2$  co-doped with Xe and  $O_2$ , in which, in addition to ionic XeO centers, the atomic  $O(^1S \rightarrow ^1D)$  transition with a radiative lifetime of 50  $\mu s$  is observed. The photogeneration of the atomic centers and the stability of the atomic and molecular emissions are sensitive to sample preparation and thermal and irradiation histories. In annealed solids at temperatures below 6.5 K the atomic emission does not bleach, implying that the vertically prepared  $O(^1D)$  atoms undergo intersystem crossing to form  $O(^3P)$  rather than react with  $D_2$ . The barrier to insertion on the  $O(^1D) + D_2$  potential energy surface in solid  $D_2$  is explained as a many-body polarization effect. The recombination of  $O(^3P)$  atoms can be initiated thermally and can be monitored by their thermoluminescence at the molecular  $O_2(A' \rightarrow X)$  transition. The thermal onset of recombination varies between 5.5 K and 9 K, depending on the sample preparation method. In all cases, the thermally induced recombination is catastrophic, accompanied by thermal runaway, pressure burst, and material loss. This is interpreted as an indication that the process is initiated by self-diffusion of the host, consistent with the notion that atomic O centers stabilize the host lattice. © 2000 American Institute of Physics. [S1063-777X(00)00709-X]

### 1. INTRODUCTION

Oxygen-doped solid hydrogen and its isotopes provide an opportunity for the study of photophysics and -chemistry in quantum hosts. In addition to fundamental motivations, solid hydrogen doped with atomic oxygen is a prototype of a mono-propellant, which, with optimized dopant concentration, could have a significantly enhanced specific impulse over the standard liquid oxygen/hydrogen mix presently used as rocket fuel.<sup>1</sup> The present study was motivated by the absence of the rudimentary data required to assess the possibility of this concept.<sup>2</sup> Our experimental studies show the stability of atomic oxygen with respect to diffusion, and, more significantly, we uncover the non-reactivity of both ground-state and electronically excited atomic oxygen with the  $D_2$  host. Reports of these findings have appeared as conference proceedings<sup>3</sup> and in a thesis.<sup>4</sup> Here, we collect some of the more important observations, which have served as the basis for theoretical analyses that have already been published.<sup>5,6</sup>

The experimental plan is based on our prior studies of atomic and molecular oxygen in rare gas solids.<sup>7–9</sup> The *in situ* photogeneration of atomic oxygen, by ArF laser irradiation of  $O_2$ -doped solid hydrogen at 193 nm, is the proposed starting point. Note that, although this radiation provides an energy 1.3 eV in excess of the dissociation limit of the molecule, the strong cage effect in rare gas solids prevents dissociation of the molecule, and the recombinant

emission over the various electronic states that correlate with  $O(^3P) + O(^3P)$  is observed.<sup>10,11</sup> Due to the light mass and weak forces in the hydrogen quantum solid, we would expect significantly reduced stopping power of the host. Whether  $O_2$  will undergo facile photodissociation under 193 nm irradiation in solid hydrogen is the first question of interest. Quite clearly, in addition to the different kinematics of quantum versus classical solids, now reactive channels for the formation of OH and  $H_2O$  are open to the photodissociation of  $O_2$ . The laser induced fluorescence (LIF) probes used in our experiments give no evidence as to the presence of these reactive channels; we only detect molecular and atomic oxygen, and in both cases only a fraction of the population is detected. We have previously reported on the spectroscopy of molecular  $O_2$  isolated in solid hydrogen and deuterium.<sup>12</sup> We rely on the orbitally forbidden  $A'(^3\Delta_u) - X(^3\Sigma_g^-)$  transition, known as the Herzberg III band,<sup>13</sup> as the laser-induced fluorescence probe of the isolated molecules. This transition gains its intensity by matrix-induced mixing between  $O_2(A')$  and the nearby repulsive  $O_2(^3\Pi)$  state. Based on the symmetry requirements for the mixing, we have argued that only molecules isolated in fcc sites and oriented along the [111] axis of the unit cell are observable. Only a fraction of the molecules are observable in solid  $D_2$ , and none are detectable in solid  $H_2$ , although the presence of the isolated molecules could be verified there by thermal cycling of solids

over-coated with a film of Xe. It was inferred that in solid  $H_2$  the guest  $O_2$  molecules are exclusively isolated in hcp sites. This consideration is the main reason for carrying out the present studies in solid  $D_2$ , in which metastable fcc sites can be produced via thermal cycling. In rare gas solids both atomic and molecular oxygen can be monitored through fluorescence induced by laser irradiation at 193 nm. The same applies in solid  $D_2$ , although, as will be argued, this non-resonant probe is also limited to detection of special sites. Nevertheless, the availability of a method of monitoring O atoms, via its  $O(^1S \rightarrow ^1D)$  emission, allows verification of its photogeneration and permits drawing direct conclusions with regard to chemical stability and thermally induced recombination. As will be discussed, we find the concept of an atomic impurity diffusing through the solid lattice to be misguided. The more surprising result is the absence of chemistry on the  $O(^1D) + H_2$  potential energy surface, which in gas phase binary collisions would lead to formation of  $OH + H$  (Ref. 14), but in the presence of a third body should form  $H_2O$ . According to the most refined potential energy surfaces the gas phase reaction is barrier-free.<sup>15</sup> To ensure that the solid state observations of non-reactivity were not a peculiarity of the special sites probed, we carry out measurements in solid  $D_2$  co-doped with  $O_2$  and Xe, in which Xe acts as a sensitive detector of atomic oxygen in its various electronic states.<sup>16</sup> These studies more definitively confirm the chemical stability of  $O(^1D)$  in solid  $D_2$ . This unexpected result could not be rationalized in molecular dynamics calculations using refined, non-additive, but covalent pair potentials.<sup>6</sup> However, the more recent theoretical treatment, using the diatomics-in-molecules approach, which takes into account the ionicity of interactions, succeeds in providing a rationale for the many-body origin of the reaction barrier.<sup>17</sup> Here we provide the experimental data that has inspired these theoretical developments.

## 2. EXPERIMENTAL

We prepare the doped films by spray-deposition of pre-mixed gaseous samples on an oxygen-free copper substrate, mounted on the cryotip of a He flow-cryostat (see schematic in Fig. 1). The cryostat is contained in an all-stainless-steel, ultrahigh-vacuum shroud fitted with metal-sealed  $MgF_2$  and sapphire windows. A silicon diode of  $\pm 0.05$  K accuracy (Lakeshore Cryotronics) mounted on the back of the copper substrate, is used for temperature measurements. The shroud is evacuated with a turbomolecular pump to a base pressure below  $10^{-8}$  Torr at room temperature. The samples are deposited at temperatures ranging from 3.8 K to 5.5 K, with film growth rates ranging from 1.6  $\mu\text{m}/\text{min}$  to 3.6  $\mu\text{m}/\text{min}$ . The sample thickness is measured during deposition by monitoring interference fringes from a reflected He:Ne laser. Typical film thicknesses vary from 50 to 100  $\mu\text{m}$ . The films are transparent to the eye.

Emission from the sample is recorded using either an optical multichannel analyzer (Princeton Applied Research OMA3) equipped with a 0.25-m polychromator, or using a photomultiplier (Hamamatsu R-666) after dispersing the radiation through a 0.75-m monochromator (Spex). A digitizing/averaging scope (Tektronics 2430) is used to record transients, which are then transferred to a personal

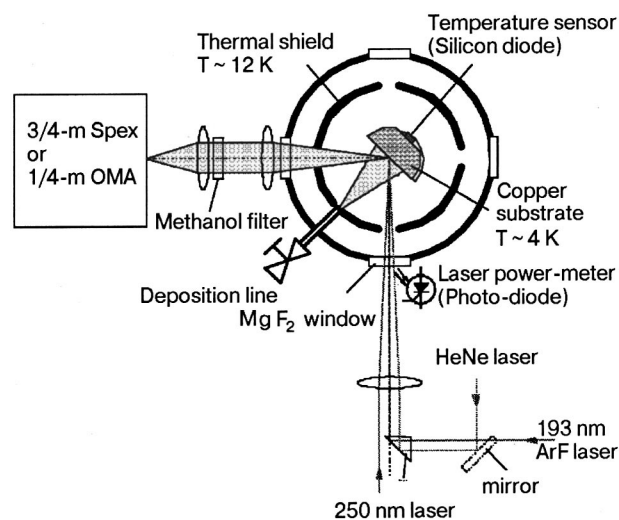


FIG. 1. Experimental setup. The He flow cryostat is adapted for simultaneous monitoring of fluorescence induced by the 193 nm laser and the doubled dye laser from the same interrogation volume. The temperature of the cryotip is monitored with a Si diode, the output of which is read out by the computer, along with the fluorescence and thermoluminescence data. The He:Ne laser is used to monitor thickness of the growing film; otherwise the films are invisible to the eye.

computer for further data analysis. The same computer is also interfaced to the temperature sensor/controller and the time delay generator used to synchronize the lasers.

As excitation source, the doubled output of an excimer-pumped dye laser and/or the direct output of an ArF laser operating at 193 nm is used. In many of the experiments the two lasers are synchronized to correlate resonantly induced fluorescence from the molecules with the 193-nm-induced chemistry and fluorescence of atomic and molecular oxygen.

## 3. RESULTS

### 3.1. $O_2$ -doped solid $D_2$

The majority of experiments were performed in oxygen-doped solid deuterium samples with a gas mix composition of 1:500. Excitation of  $O_2/D_2$  samples at 193 nm leads to emission on both molecular  $O_2(A'^3\Delta_u \rightarrow X^3\Sigma_g^-)$  and atomic  $O(^1S \rightarrow ^1D)$  transitions, as shown in Fig. 2a. The fluorescence lifetime of the molecular emission is 5.4  $\mu\text{s}$ , while that of the atomic emission at 559 nm is 230  $\mu\text{s}$  (measured at 4 K). In addition to this LIF scheme, the photogeneration of O atoms can be verified through their thermoluminescence (TL). The thermally driven recombination of atoms,  $O(^3P) + O(^3P)$ , produces the same  $A' \rightarrow X$  spectrum, as shown in Fig. 2b. The same emission spectrum is obtained through resonant  $A' \leftarrow X$  excitation of the molecule, as previously described in some detail.<sup>12</sup> Note that the fluorescence yield of the resonant excitation depends on structural changes of the solid, since it probes only a sub-ensemble of molecules in fcc sites. Also, the 193-nm-induced molecular emission is contingent upon cage-induced recombination of the atoms and is therefore not a direct probe of the molecular concentration. Further, the excitation resonance responsible for the 193-nm-induced atomic emission is not clear. We can establish that the atomic emission arises from a broad structureless absorption. This is illustrated in Fig. 3 and contrasted

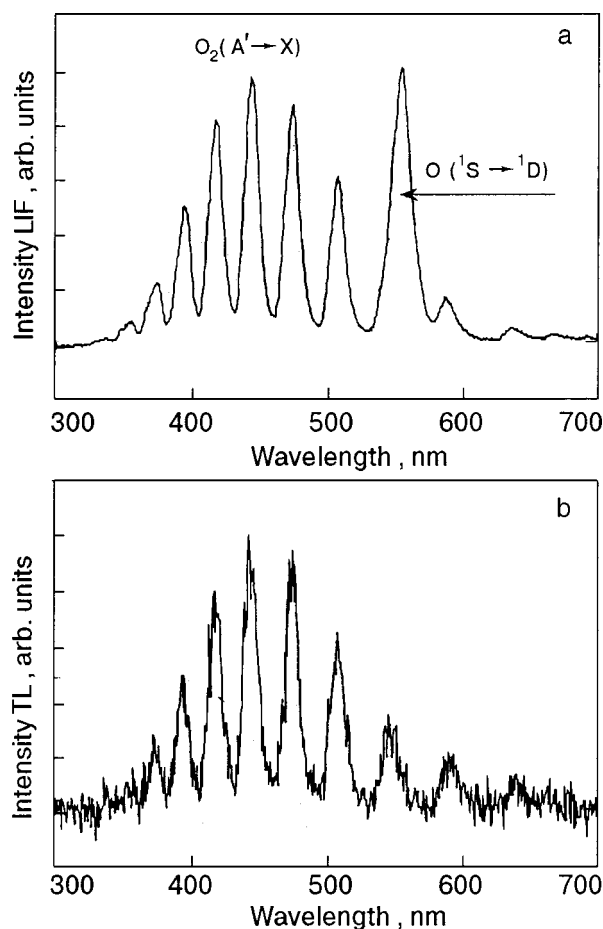


FIG. 2. Laser induced fluorescence (a) and thermoluminescence (b) from  $O_2$  doped  $D_2$  solids irradiated at 193 nm. The atomic  $O(^1S \rightarrow ^1D)$  emission, at 559 nm, appears in the laser induced fluorescence spectrum in (a).

with the sharp molecular resonances in the same spectral range. A search for direct access of the emitting atomic state, via the forbidden  $^1S \leftarrow ^3P$  transition near 297 nm, failed. Thus, the 193 nm probe of the O atoms is also indirect and, as will be shown below, not a quantitative probe of the atom concentration in the solid.

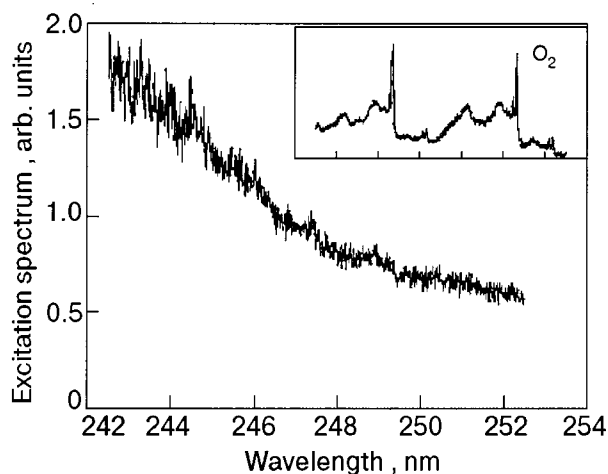


FIG. 3. Excitation profile of the atomic  $O(^1S \rightarrow ^1D)$  emission. In the inset, the excitation spectrum for the molecular  $O_2(A' \rightarrow X)$  emission is shown.

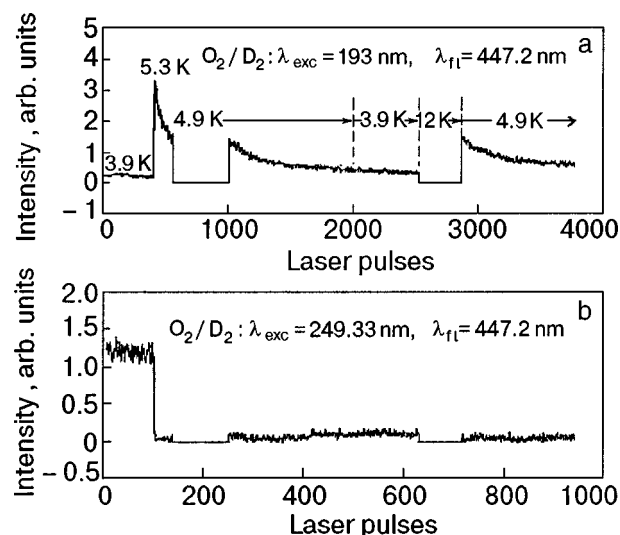


FIG. 4. Thermal and irradiation histories of molecular laser induced fluorescence in a quench-condensed solid. The sample, 0.2%  $O_2$  in solid  $D_2$ , was deposited at 3.8 K. The temperature is varied during irradiation, and its history is indicated in (a). The flat regions centered at 200 and 700 pulses of the 249 nm laser correspond to periods where the laser beams were blocked off.

To correlate the thermal and irradiation histories of the atomic and molecular fluorescence, we simultaneously monitor LIF from the 193 nm laser and the doubled dye laser. The latter is tuned to the molecular  $A'(v' = 8) \leftarrow X(v'' = 0)$  resonance at 249.33 nm, the lasers are delayed by 1 ms relative to each other, and the fluorescence is gate-detected to distinguish the various contributions. Figures 4 and 5 illustrate typical histories in “quench”-condensed samples, prepared by slow deposition at 3.8 K, the lowest temperature of the cryostat. The data illustrate that:

a) In the freshly deposited samples, at 3.9 K, 193 nm irradiation does not cause a measurable change in either the resonantly induced  $O_2$  emission (Fig. 4), or in the 193 nm induced atomic and molecular emissions (Fig. 5).

b) Upon warming the sample to 5.5 K with continued irradiation, a sudden, tenfold growth in the 193-nm-induced molecular and atomic emissions are observed. This is accompanied by a sudden 90% loss of the resonantly induced molecular emission. This sudden transition suggests gross structural change in the lattice. With continued irradiation, the 193-nm-induced emission decays in time, while the resonantly induced emission does not recover. Clearly, the  $O_2$  molecules probed by the two different lasers belong to two different ensembles. The 193-nm-induced the emission intensity remains constant decay is verified to be laser aided, by noting that when the irradiation is interrupted. The level to which the emission decays is temperature dependent. When the temperature is lowered to 4 K, the emissions subside to pre-warmup level.

c) The resonantly induced molecular emission does not respond when the warm-up cycle is repeated (Fig. 4). The 193-nm-induced molecular emission repeats its behavior (Fig. 5b), and the atomic emission does not fully regenerate in subsequent cycles (Fig. 5a).

d) Note the thermal runaway at 5.3 K, as evidenced by the temperature spikes in Fig. 5c. They repeat at the same

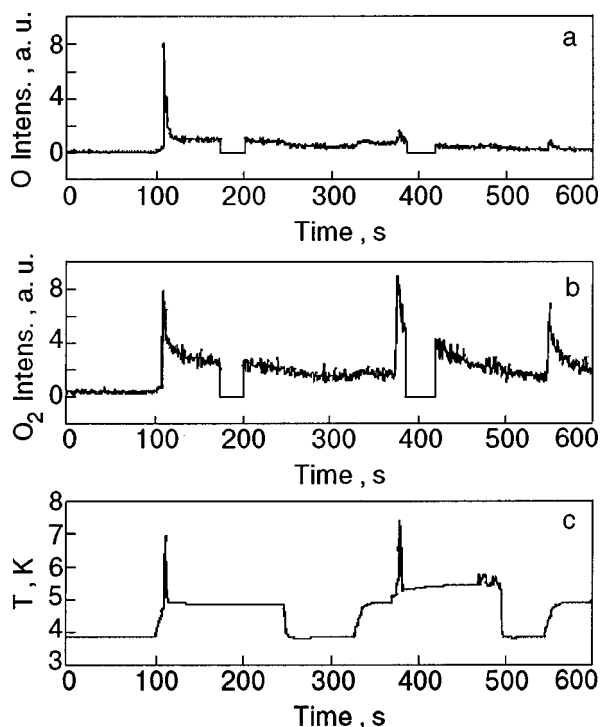


FIG. 5. Thermal and irradiation histories of 193-nm-induced atomic (a) and molecular (b) fluorescence in the quench-condensed solid (0.2% O<sub>2</sub> in solid D<sub>2</sub>). The thermal runaway spike is associated with gross change in the morphology due to phase transition of islands in the solid (c).

temperature and are clearly independent of the atom content of the solid. This behavior is consistent with the known reversible, hysteretic phase transition of quench-condensed solid deuterium.<sup>18</sup> The initial 90% drop in the resonantly induced molecular fluorescence can therefore be understood as due to an fcc-to-hcp phase transition in crystallites. The transition evidently generates sites in which the 193-nm-induced O<sub>2</sub> fluorescence is observed.

A substantively different behavior is observed in samples deposited at higher temperature, between 4.5 K and 5.5 K. An example is shown in Fig. 6 for a sample deposited at 5 K, annealed at 9 K, then slowly cooled to 4.4 K to start the radiation process. A correlated growth of both atomic and molecular fluorescence is observed upon 193 nm irradiation at 4.4 K. As the temperature is increased to 6 K with continued irradiation, both atomic and molecular emissions grow. As long as the temperature is held constant, these emissions remain stable at this level.

In principle, glow curves obtained by a programmed temperature ramp should enable the characterization of diffusion and recombination kinetics of atoms. This method has previously been implemented successfully for atomic oxygen in rare gas solids.<sup>8</sup> We have failed to obtain any meaningful glow curves in solid D<sub>2</sub>. The recombination occurs suddenly, leading to a flash that lasts only  $\sim 10 \mu\text{s}$ . The flash is always accompanied by a temperature and pressure surge, similar to the laser-induced fluorescence spikes shown in Fig. 5. The temperature at which the catastrophic recombination occurs depends on the gross sample morphology, determined mainly by sample deposition conditions. In samples prepared by slow deposition at 3.8 K, the recombination occurs between 5.5 K and 7.5 K. In samples deposited at somewhat

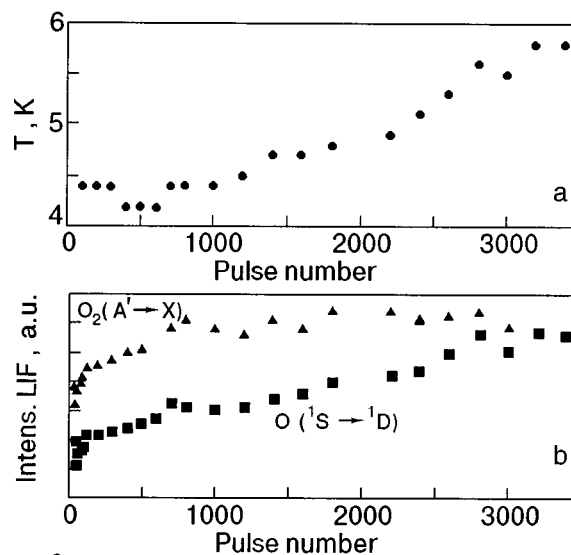


FIG. 6. Thermal (a) and irradiation (b) history of an O<sub>2</sub>:D<sub>2</sub> sample deposited at 5 K and annealed at 9 K prior to irradiation. The data points are the 193-nm-induced fluorescence from O and O<sub>2</sub> as a function of the number of laser pulses.

higher temperatures, 4.5 K–5.5 K, and at a deposition rate of  $\sim 3 \mu\text{m}/\text{min}$ , the recombination occurs at a temperature between 7 K and 9 K. In samples which are pre-annealed at 9 K, then cooled to 4 K and irradiated, the TL is observed at temperatures as high as 11 K.

### 3.2. N<sub>2</sub>O-doped solid N<sub>2</sub> and neat solid O<sub>2</sub>

Extensive 193 nm irradiation of N<sub>2</sub>O doped solid N<sub>2</sub> (M/R=1:1000) and neat solid O<sub>2</sub> did not produce any detectable emission from atomic O. Given the fact that N<sub>2</sub>O dissociates readily in solid N<sub>2</sub> (Ref. 19), the absence of 193-nm-induced O atom emission supports the notion that the atomic LIF observed in solid D<sub>2</sub> arises from special centers. The absence of 193-nm-induced atomic emission in solid O<sub>2</sub> establishes that the observed emission in solid D<sub>2</sub> is not from clusters of O<sub>2</sub>.

### 3.3. Solid D<sub>2</sub> co-doped with O<sub>2</sub> and Xe

To avoid the uncertainty of LIF detection of O atoms in solid D<sub>2</sub>, we carried out a set of studies in ternary solids prepared at a mole ratio of 1:5:500O<sub>2</sub>:Xe:D<sub>2</sub>. After depositing the samples at 5 K, the O<sub>2</sub> excitation spectra were investigated with the doubled dye laser. The excitation and emission spectra of O<sub>2</sub> are identical to those obtained in the absence of Xe, indicating that only isolated molecules are interrogated in both cases. This is consistent with the fact that the A' → X emission is quenched by Xe. Excitation at 193 nm immediately produced a bright emission from XeO centers, as illustrated in Fig. 7. The molecular fluorescence induced at 193 nm, which was the dominant feature in the O<sub>2</sub>/D<sub>2</sub> samples (see Fig. 2) is practically absent in the spectrum of Fig. 7. The spectrum now consists entirely of atomic emissions. In the time-integrated spectrum, the O(1S → 1D) emission can clearly be identified. While the peak is virtually unshifted at 559 nm, the effect of Xe is to reduce the radiative lifetime to 50  $\mu\text{s}$  (230  $\mu\text{s}$  in D<sub>2</sub>). Thus, it may be more

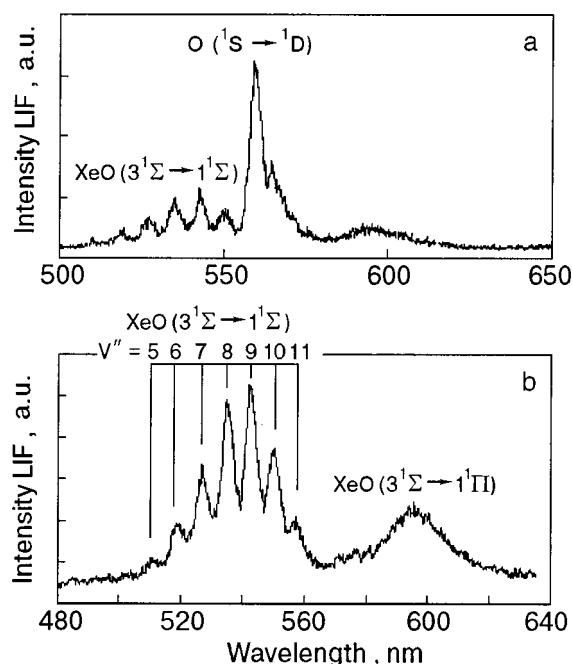


FIG. 7. Fluorescence spectrum obtained with 193 nm irradiation of solid  $D_2$  co-doped with  $O_2$  and Xe ( $O_2$ :Xe: $D_2$ =1:5:500). The spectrum (a) is obtained with time integration, the spectrum (b) is obtained with a 100 ns gate. All features in the spectrum (b) have the same lifetime of  $(130 \pm 5)$  ns, while the atomic oxygen emission (a) has a lifetime of  $50 \mu s$ .

appropriate to assign this transition to  $XeO(2^1\Sigma \rightarrow 1^1\Sigma)$  (Ref. 20). In addition, a vibrational progression centered at 530 nm and a broad band at 590 nm are observed. Both of these emissions have lifetimes of  $(130 \pm 5)$  ns. Accordingly, they can be separated from the atomic emission by gated detection, as shown in Fig. 7b. With the help of the Xe–O potential energy curves illustrated in Fig. 8, the nature of these emissions can be identified with some confidence.<sup>21</sup> Given that the vibrational progression and the band at 590 nm have the same lifetime, they are likely to originate from

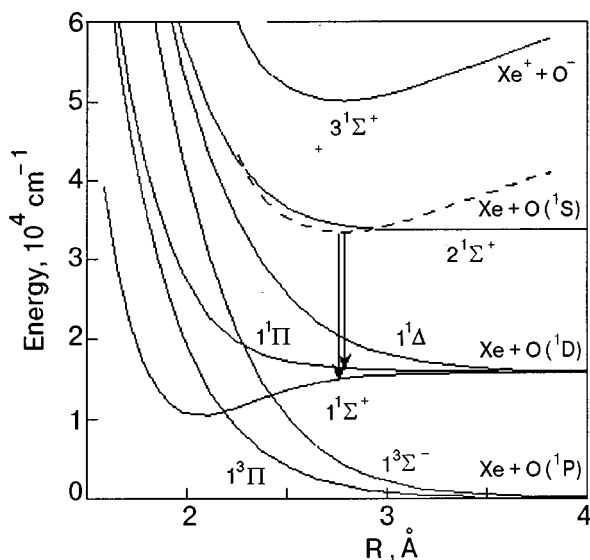


FIG. 8. The gas phase XeO potentials and the required placement of the upper emitting state (dashed line) in the fluorescence spectrum of Fig. 7. Note that a double minimum is implied to arise from the mixing between  $3^1\Sigma$  and  $2^1\Sigma$  potentials.

the same upper state. Given their short radiative lifetime, they can be confidently assigned to the  $Xe^+O^- \rightarrow XeO$  charge transfer transitions. Given that only the  $XeO(1^1\Sigma)$  state, which correlates with  $O(^1D) + Xe(^1S_0)$ , is deep enough to sustain the vibrational progression, the transition can safely be assigned to  $Xe^+O^-(3^1\Sigma) \rightarrow XeO(1^1\Sigma)$ . This would then suggest that the broad emission at 590 nm is due to  $Xe^+O^-(3^1\Sigma) \rightarrow XeO(^1\Pi)$ . In both cases the terminal state of the transition correlates with  $O(^1D) + Xe(^1S_0)$ . The vibrational progression seen here is quite similar to that observed for XeO in solid Ar,<sup>22</sup> and the numbering is simply taken from there.

We monitored the 193-nm-induced fluorescence of the atomic centers as the samples were warmed up. The emission stays nearly constant up to 12 K, and permanently decays as  $D_2$  starts to evaporate. These samples do not show significant TL, presumably because  $O_2(A')$  is quenched by Xe. All recombination must occur at Xe sites as the  $D_2$  evaporates.

## 4. DISCUSSION

### 4.1. The non-reactivity of $O(^1D)$

The interpretation of the experiments in  $O_2/Xe/D_2$  is the most direct with regard to the chemical stability of atomic oxygen in its various electronic states in solid  $D_2$ . The observation of the molecular resonant excitation immediately after deposition establishes the presence of isolated molecules. Subsequent irradiation at 193 nm generates the O and XeO emissions without a trace of the molecular spectrum. We may conclude that  $O_2$  can be photodissociated in solid  $D_2$  by 193 nm irradiation. Despite the excess energy of 1.3 eV, the impulsively generated  $O(^3P)$  atoms survive in the  $D_2$  host. The absence of any 193-nm-induced recombinant molecular fluorescence is a good indication that the cage is ineffective in solid  $D_2$ .

The O atoms scavenged by Xe are interrogated via the XeO charge transfer transitions, which can be assigned with some confidence. They invariably terminate on the  $O(^1D) + Xe$  potential energy surface. We can be sure that the O: Xe pair is surrounded by  $D_2$ , since in Xe clusters the XeO emissions occur at 740 and 370 nm.<sup>7</sup> The fact that the XeO transitions do not bleach with extended irradiation, establishes that the photogenerated  $O(^1D)$  atoms do not react with the host.

It would seem that the proximity of Xe atoms is sufficient to generate a barrier toward the  $O(^1D) + D_2$  reaction. This barrier cannot be due to the binding between  $O(^1D)$  and Xe, since, at least in the 559 nm transition, which is red-shifted from the gas phase value of 557.7 nm, the transition must terminate on the flat part of the interaction potential. The perturbation that may be ascribed to Xe is the change in transition dipole of the atomic  $1S \rightarrow 1D$  emission, evidenced by the shortening of the radiative lifetime to  $50 \mu s$ . The origin of this perturbation is well understood to be due to the ionicity of the  $XeO(2^1\Sigma)$ , which is derived by mixing with the  $Xe^+O^-(3^1\Sigma)$  charge transfer state. Indeed, to rationalize the observed emission spectra of the charge transfer states, we must conclude that due to solvation in the polarizable medium, the  $Xe^+O^-(3^1\Sigma)$  and  $XeO(2^1\Sigma)$  potentials are strongly mixed. The situation is quite similar to that of XeO

in solid Ar (which has polarizability similar to that of H<sub>2</sub>), for which we had suggested the creation of a double minimum due to the crossing of the solvated Xe<sup>+</sup>O<sup>-</sup>(3<sup>1</sup>Σ) and XeO(2<sup>1</sup>Σ) potentials.<sup>7</sup> This is shown schematically in Fig. 8. Note that the double minimum can arise by mixing between the charge transfer and covalent state, rather than the creation of an actual crossing which would require the lowering of the Xe<sup>+</sup>O<sup>-</sup>(3<sup>1</sup>Σ) state by ~1.5 eV.<sup>21</sup> The fact that the radiative lifetime of the transition is 130 ns is sufficient to identify the nature of the transition as that of charge transfer, and therefore the upper state as Xe<sup>+</sup>O<sup>-</sup>. Why would this prevent chemistry on the terminal O(<sup>1</sup>D)+D<sub>2</sub> surface? We surmise that the partial charge in Xe<sup>δ+</sup>O<sup>δ-</sup> prevents the formation of the O–H bond, which can only proceed by developing positive charge on the targeted hydrogen molecule. In effect, the partial charge transfer on the Xe+O(<sup>1</sup>D) can be thought to create a polarization barrier. This is the essence of the theoretical analysis of O-doped solid H<sub>2</sub> which we consider next.<sup>17</sup>

Consider the O(<sup>1</sup>S→<sup>1</sup>D) transition in D<sub>2</sub> in the absence of Xe. Independent of the excitation channel, since this emission does not bleach, we have to conclude that atomic oxygen in all of its electronic states, and in particular in its <sup>1</sup>D state, does not react with the host. This, at first, seems at odds with the well-established fact that the O(<sup>1</sup>D)+H<sub>2</sub> surface does not contain a reaction barrier. The diatomic molecules (DIM) calculations of Kunz, in which O(H<sub>2</sub>)<sub>n</sub> is considered with the explicit inclusion of the ionic manifold of states for the cluster, show the many-body nature of the barrier.<sup>17</sup> The picture is as follows: The O(<sup>1</sup>D)–H<sub>2</sub> interaction gains its binding character due to its ionicity. When in the middle of an octahedral array of H<sub>2</sub> molecules, the central O atom can mix with the charge transfer states of all neighbors. The insertion coordinate, however, requires the localization of charge on one hydrogen molecule to reach the ionicity of the O–H bond in its H–O–H transition state. The barrier arises as the energy of localization of the excited state charge density, from the 12 nearest neighbors to one molecule. The charge distribution in the excited state is mirrored by the polarization on the <sup>1</sup>D surface. In effect, the polarization barrier centers the O atom in the cubic site and prevents the reaction. In the absence of the many, there is no barrier. To our knowledge, this is the most direct demonstration of a many-body-potential control of chemical dynamics.

#### 4.2. Nonresonant excitation mechanism: O<sub>2</sub>(X):O(<sup>3</sup>P) centers

Although 193-nm-excitation is used to follow both O and O<sub>2</sub> in solid D<sub>2</sub>, the mechanism of this excitation is indirect, preventing quantitative determinations of impurity concentrations and photodissociation yields. The excitation spectrum in Fig. 3 indicates that the atoms are accessed through a broad band that cannot be ascribed to the isolated atom but rather to an M–O adduct, similar to the charge transfer states of Xe–O. Similarly, the observation that the 193-nm-induced molecular emission grows with irradiation time, as seen in Fig. 6, clearly indicates that we are not simply interrogating the molecular concentration. The close correlation of the thermal and irradiation histories of 193-nm-induced O and O<sub>2</sub> emissions suggests a common origin.

The most consistent assignment that can be offered is that the absorption is due O<sub>2</sub>(X):O(<sup>3</sup>P) pairs, distinct from ozone. Since both O and O<sub>2</sub> are present in the sample, O<sub>3</sub> can be formed. However, the excitation wavelengths used, 193 nm–255 nm, do not have the requisite energy to produce O(<sup>1</sup>S) from the ground state of ozone, and cannot therefore explain the LIF signal over the O(<sup>1</sup>S→<sup>1</sup>D) transition. The main dissociation channel of ozone in this excitation range is the production of O(<sup>1</sup>D).<sup>19</sup> As in the case of N<sub>2</sub>O and O<sub>3</sub> isolated in rare gas solids, we expect that ozone would undergo facile photodissociation in solid D<sub>2</sub>. Even though the magnitude is difficult to obtain with confidence, *ab initio* calculations invariably show an angle dependent potential barrier to formation of O<sub>3</sub> from O<sub>2</sub>(X):O(<sup>3</sup>P).<sup>23,24</sup> A continuous excitation spectrum, starting near 250 nm, can then be ascribed to absorption over the dense manifold of intermolecular O<sub>2</sub>–O potentials, from which branching to O<sub>2</sub>+O(<sup>1</sup>S) and to O<sub>2</sub>(A') + O is to be expected.

The above consideration complicates the interpretation of the 193-nm-driven photodissociation yields of O<sub>2</sub> in solid D<sub>2</sub>. The samples containing Xe indicate facile dissociation, accompanied by migration of O atoms to reach the Xe sites. In the absence of Xe we cannot establish photodissociation probabilities or, equivalently, the caging efficiency of the host, since the observed atomic and molecular densities can entirely be attributed to special centers. Indeed, in samples where LIF from the atomic centers is nearly absent, a strong thermoluminescence is observed upon warm-up, indicating that only a fraction of the O atoms are spectroscopically detected. Nevertheless, it is clear that chemistry, namely formation of H<sub>2</sub>O, is not a significant channel in the dissociative excitation of O<sub>2</sub>.

#### 4.3. Thermally induced recombination

The thermally induced recombination of oxygen atoms in solid D<sub>2</sub> differs fundamentally from what is observed in the classical rare gas solids. There, it is always possible to ramp up the temperature at a rate at which the glow curve can be measured, to extract the diffusion kinetics of impurities in the solid. This is not possible in the solid hydrogens. Instead of a glow curve, we obtain a sudden flash, accompanied by an uncontrollable thermal runaway and pressure surge. In effect, the host diffuses around the impurities. The theoretical analysis of O-doped solid hydrogens gives a useful perspective.<sup>6</sup> Due to the deeper guest–host potential, hydrogen molecules are significantly more localized near the impurity site. In fact, a linear increase in the density of the solid is predicted as a function of concentration of O atoms. In effect, the O atoms are coated with a layer of hydrogen, which is less mobile than the bulk. It would therefore be difficult to imagine the coated impurity diffusing while the host retains its integrity as a solid. The experimental observation is rationalized as the fusion of O centers in a solid undergoing gross structural change due to self-diffusion of the host, with the recombination energy of the guests serving as positive feedback for the thermal runaway.

## 5. CONCLUSIONS

Atomic oxygen can be photogenerated *in situ* in solid D<sub>2</sub> by photodissociation of molecular oxygen. The atomic centers in such a solid are stable, both chemically and physically. The non-reactivity of O(<sup>1</sup>D) with the host is particularly striking, and rationalized to result from a polarization barrier of strictly many-body origin.<sup>17</sup> In pre-annealed samples, the atomically doped solids have been shown to be stable up to  $T=11$  K. Indeed, in earlier simulations it had been argued that atomic oxygen stabilizes the host lattice and increases its density.<sup>6</sup> This is indirectly verified in the present, study by recognizing that O atoms recombine only after the host loses its integrity as a solid. Thus this exploratory study seems to resolve some of the more rudimentary issues with regard to the consideration of oxygen-doped solid hydrogen as a propellant. In this regard, the experiments do not provide a reliable estimate of the concentration of atomic centers or the achievable doping levels, considerations crucial to assess specific impulse.

The spectroscopy, photodynamics, and photophysics of impurities in solid hydrogens raise many fascinating questions. A more quantitative study of the very system we have described, for example by combining IR and visible methods, would be quite useful. The present studies remain qualitative with regard to several important questions. With regard to the caging ability of the solid, based on the O<sub>2</sub>:Xe:D<sub>2</sub> experiments, we believe it to be small. Based on the thermal and irradiation histories of fluorescence we have postulated the presence of O<sub>2</sub>(X):O(<sup>3</sup>P) pairs that do not form ozone. Infrared studies could nicely resolve this issue. More generally, solid hydrogen could be used as an ideal nonperturbing medium of weak forces to investigate intermolecular potential energy surfaces.<sup>25</sup> Finally, in the present study the effects of ortho- and parahydrogen have been completely neglected. They need not be invoked to explain any of the observations, and it is believed that due to the paramagnetic nature of the impurities, at the concentrations of impurities used, the solid host is entirely in the ground spin state.

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