

# Photodynamics in oxygen doped solid deuterium

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A spectroscopic investigation of O<sub>2</sub> isolated in D<sub>2</sub> matrices is reported. Standard matrix isolation methods lead to only a small observable concentration of isolated molecules in D<sub>2</sub> and fail in the case of H<sub>2</sub>. Both resonant excitation of the molecule over the  $A'(^3\Delta_u) \leftarrow X(^3\Sigma_g^-)$  transition, and dissociative pumping at 193 nm, lead to vibrationally relaxed  $A' \rightarrow X$  emission, with a lifetime of 5.4  $\mu$ s. Independent of the initial  $\Omega$  component accessed, the fluorescence is polarized with a polarization ratio of  $1.25 \pm 0.05$ ; indicating that O<sub>2</sub> does not rotate and that the transition gains its intensity by crystal field induced mixing between the  $^3\Delta_u$  and a nearby  $^3\Pi_u$  state. This uniquely identifies the anisotropy of the local field as  $Y_{43} + Y_{4-3}$ , which in turn implies that the molecule is trapped in an fcc site with its axis aligned along the [111] direction. The observed zero phonon line intensities can be explained consistently if the spin-orbit multiplet is assumed to be normal, in contrast with the accepted scheme in the gas phase. The zero phonon lines of O<sub>2</sub> isolated in D<sub>2</sub>, show librational satellites with a 15 cm<sup>-1</sup> spacing in the  $A'$  state, and  $\sim 25$  cm<sup>-1</sup> spacing in the  $X$  state. Intensity analysis of these progressions leads to the conclusion that the molecular axis in the excited state is tilted relative to the ground state. Deposits in D<sub>2</sub> and H<sub>2</sub> samples overcoated with Xe, after annealing, exhibited spectra of isolated O<sub>2</sub> which are perturbed by the Xe film. © 1995 American Institute of Physics.

## I. INTRODUCTION

Frozen rare gases have been extensively used as matrices for the isolation and spectroscopic investigation of transient species. The emphasis on dynamical studies in such media, as model systems for the isolation of dynamics common to condensed phases in general, is more recent.<sup>1</sup> With the exception of He and to some extent Ne, these matrices form classical van der Waals solids. Quantum solids,<sup>2</sup> in which the single particle zero point amplitudes are significant in comparison to lattice spacings, represent novel conceptual challenges in descriptions of many-body dynamics, which are virtually unexplored. The possibility of isolating classical impurities in such media, the diffusion of a classical impurity in a quantum host, the description of interactions between guest and collective degrees of freedom of the host, effects on local and extended energetics pose fascinating questions that have not been addressed at any length. In this respect solid hydrogen represents a particularly interesting system. Even if the radioactive tritium is neglected, three isotopic species are available: H<sub>2</sub>, HD, and D<sub>2</sub> which have quite distinct properties.<sup>3-5</sup> This should enable investigation of effects of zero-point motion, tunneling, and host molecular symmetry on dynamical processes, on photophysics and chemistry. A rather complete review of work to date on this subject, *The spectroscopy and reactive dynamics of atoms trapped in molecular hydrogen matrices*, was recently given by Fajardo *et al.*<sup>6</sup>

We have initiated studies on photodynamics of oxygen doped solid deuterium, which in addition to photophysics allows the possibility of investigating photochemistry between guest and host. As a starting point, we have carried out an investigation of the molecular spectroscopy, which we report in this paper. D<sub>2</sub> was chosen after some failed attempts at observing spectra of the isolated molecule in solid H<sub>2</sub> by the standard matrix isolation techniques which we rely on. We discuss these attempts, as they may bear upon the differences between quantum and classical hosts with respect to isolation of incommensurate guests or with respect to diffusion and self-annealing of the host.

The electronic spectroscopy of oxygen isolated in rare gas solids, and in solid nitrogen is well established.<sup>7-10</sup> It exhibits interesting, isotopically dependent relaxation dynamics. Resonant or dissociative excitation of the <sup>16-16</sup>O<sub>2</sub> in the UV, above 5 eV, produces vibrationally relaxed emission over the  $A'(^3\Delta_u) \rightarrow X(^3\Sigma_g^-)$  transition, also known as the Herzberg III band. This transition, although extremely weak, has been extensively studied in the gas phase,<sup>11-16</sup> since its first observation in absorption by Herzberg.<sup>11</sup> The  $A'$  state is nested amid the  $A(^3\Sigma_u^+)$  and the  $c(^1\Sigma_u^-)$  potentials. When the temperature of the matrix is raised, in Ar, in N<sub>2</sub>,<sup>6,10</sup> and in Kr,<sup>17</sup> the  $A'$  state of O<sub>2</sub> transfers its population to the  $c$  state: the  $A' \rightarrow X$  emission subsides, and is replaced by the  $c(^1\Sigma_u^-) \rightarrow a(^1\Delta_g)$  emission. The vibrational resonance required in this process is isotopically sensitive, such that in <sup>16-18</sup>O<sub>2</sub> the  $c \rightarrow a$  emission dominates even at low temperature.<sup>7(b)</sup> The observed transitions,  $A \rightarrow X$  and  $c \rightarrow a$ , indicate that in the matrices, while spin and parity selection rules are in effect obeyed, orbital selection rules are violated. Since these orbitally forbidden transitions are enhanced by

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many orders of magnitude in the matrix environment, they can serve as sensitive probes of the local interactions and dynamics.

Several conceptual issues can be addressed via the spectroscopy of O<sub>2</sub> in quantum hosts. In the homonuclear <sup>16-16</sup>O<sub>2</sub>, the even rotational states are absent in the ground state, the molecule will therefore be found in  $J=1$  at absolute zero. Does this imply that in a soft cryogenic host O<sub>2</sub> rotates? Due to their zero-point amplitudes quantum hosts are expected to self-anneal, does this imply segregation or is it possible to prepare a nonequilibrium solid solution? What is the local structure of the host if it anneals around the impurity? D<sub>2</sub> is much lighter than the classical van der Waals atoms, does this therefore imply a weaker perturbation of the molecular states? We attempt to answer these questions through a detailed analysis of the spectra.

Finally, we note that there are several prior studies of spectroscopy in O<sub>2</sub> doped solid hydrogens. Proton beam excitation of solid H<sub>2</sub> has yielded spectra of impurity O<sub>2</sub>, the  $A' \rightarrow X$  emission can be easily seen, along with emission from  $O(^1S) \rightarrow O(^1D)$ .<sup>18</sup> Electron beam excitation has been used in solid D<sub>2</sub> to interrogate the impurity molecular content.<sup>19</sup> A broad unstructured emission observed in the 450 nm region should be interpreted as arising from O<sub>2</sub> clusters. More recently, Shevtsov *et al.* have carried out ESR studies in O<sub>2</sub> doped hydrogen to characterize self-diffusion of the host molecules.<sup>20</sup> Noteworthy in that work is the absence of ESR signals from O<sub>2</sub>, implying that the ground state electronic angular momentum is quenched in solid D<sub>2</sub>.

## II. EXPERIMENT

The matrices were grown on an oxygen free copper substrate, mounted on the cryotip of a He flow cryostat. The base temperature reached at the substrate is 5.3 K under free flow, and 3.6 K when pumping on the He with a 30 cfm mechanical pump. The cryostat is contained in an all stainless steel, ultrahigh vacuum shroud fitted with metal sealed MgF<sub>2</sub> and sapphire windows. A silicon diode of stated accuracy  $\pm 0.05$  K (Lakeshore Cryotronics), mounted on the back side of the polished copper substrate is used for temperature measurements. The shroud is evacuated with a turbomolecular pump to below  $10^{-8}$  Torr at room temperature. When cold, the cryostat is isolated from all pumps to prevent back-diffusion of hydrocarbons. Cryopumping is sufficient to maintain the vacuum in the system below the sensitivity of our ionization gauge ( $10^{-8}$  Torr).

Premixed gaseous samples are spray-deposited through a leak valve. In the majority of the experiments to be reported the composition of the gas was O<sub>2</sub>:D<sub>2</sub>=1:500. The sample thickness is measured by monitoring interference fringes from a reflected He:Ne laser. Typical film thicknesses used in these experiments vary from 30 to 100  $\mu\text{m}$ . The same apparatus was also used to carry out control measurements in various other compositions: O<sub>2</sub>/H<sub>2</sub>; O<sub>2</sub>/N<sub>2</sub>; D<sub>2</sub> multiply doped with O<sub>2</sub> and Xe; O<sub>2</sub>/D<sub>2</sub>(H<sub>2</sub>) samples overcoated with Xe.

Emission from the sample is recorded using either an optical multichannel analyzer (Princeton Applied Research OMA-3) equipped with a 0.25 m polychromator, or using a

photomultiplier (Hamamatsu R-666) after dispersing the radiation through various monochromators: either a 0.25 m (Schoeffel) or a 0.75 m (Spex) monochromator. A digitizing/averaging scope (Tektronics 2430) is used to record transients, or to operate in boxcar mode. The data are transferred through an IEEE-486 interface to a personal computer for storage and analysis. 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.

The matrix isolation technique relies on the preparation of nonequilibrium solid solutions by fast freezing of premixed gas samples.<sup>21</sup> This can be achieved by deposition conditions where self-diffusion of the host is negligible. Typically, a temperature below one-third the melting point of the solid is sufficient for this purpose. At the base temperature of our cryostat of 3.6 K this condition is in principle satisfied for H<sub>2</sub> ( $T_{\text{MP}}=13.8$  K). Nevertheless, our initial attempts at recording spectra of O<sub>2</sub> isolated in H<sub>2</sub> have failed. Stable films of D<sub>2</sub> ( $T_{\text{MP}}=18.6$  K) could be prepared with sufficient densities of isolated monomeric O<sub>2</sub> to enable the spectroscopic studies described below. Although we typically deposit a gas mixture of O<sub>2</sub>:D<sub>2</sub>=1:500, comparison of the signal intensity to that of O<sub>2</sub> isolated in N<sub>2</sub> matrices prepared under identical conditions, suggested that (assuming comparable quantum yields) the concentration of the observed O<sub>2</sub> isolated in D<sub>2</sub> matrices was of order 1–10 ppm.

The deposition rate was found to be a critical parameter in the preparation of these solids. Under slow deposition conditions,  $<1.5$   $\mu\text{m}/\text{min}$ , with a background pressure of  $5 \times 10^{-7}$  during deposition, structurally unstable films result when depositing below 3.8 K. After a film thickness of  $\sim 1$   $\mu\text{m}$ , the pressure in the chamber starts to oscillate wildly, presumably due to breaking-off of pieces of the “quenched-condensed” solid. A sharp transition in this behavior is observed. Upon raising the temperature above 3.8 K, the growth stabilizes. Slow deposition at temperatures below 4 K leads to thermally unstable trapping sites. Upon annealing such matrices to 5.5 K, nearly all of the laser induced fluorescence from monomers is permanently lost, presumably due to defect induced diffusion and clustering of the guest molecules. Reproducibly better isolation, and thermally stable films result at faster deposition rates,  $\geq 2.5$   $\mu\text{m}/\text{min}$ , with substrate temperatures held nominally between 3.8 and 5.3 K. Under these conditions the pressure in the vacuum shroud remains stable,  $\sim 5 \times 10^{-6}$  Torr during deposition. Such films can be heated up to 7–9 K without any appreciable diffusion and loss of the isolated guests.

To further improve the thermal stability of the films, we have tested the possibility of overcoating them with Xe. Isolated O<sub>2</sub> spectra in such solids could be recorded after heat cycling them up to  $\sim 20$  K. The spectra obtained after such a thermal cycle indicated, however, that the emissions occur from molecules near the Xe film. Interestingly, in samples where initially no emission could be observed, upon overcoating and heat cycling, monomeric oxygen spectra could be obtained. In this way it was also possible to obtain LIF in overcoated H<sub>2</sub> films.

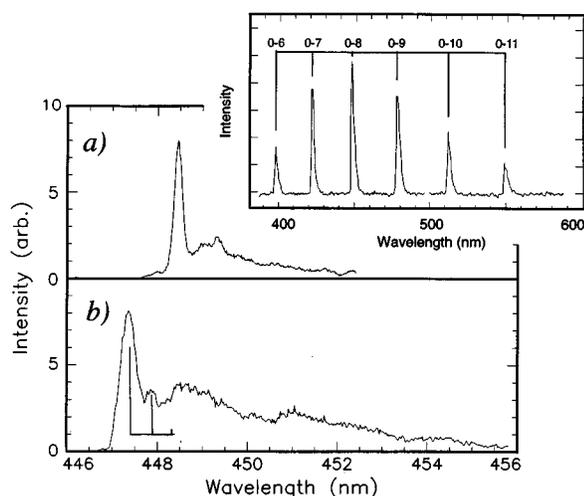


FIG. 1. Emission spectrum of O<sub>2</sub> isolated in solid D<sub>2</sub> (inset) and an expansion of the 0–8 transition. (a) In solid N<sub>2</sub>, obtained by excitation at 251.217 nm; (b) In solid D<sub>2</sub> excited at 249.328 nm. In both cases the dilution is 1:500 and  $T=4.9$  K. The stick spectrum in (b) inset is the predicted Franck-Condon progression for librations.

### III. RESULTS

Whether resonantly excited over  $A'(^3\Delta_u \leftarrow X^3(\Sigma_g^-))$  vibronic transitions, or excited to the molecular continuum at 193 nm, the same emission spectrum is obtained for O<sub>2</sub> isolated in solid D<sub>2</sub>. The spectrum, which is shown in the inset to Fig. 1, is easily assigned to the vibrationally relaxed  $A' \ ^3\Delta_u \rightarrow X \ ^3\Sigma_g^-$  transition. The  $v'=0 \rightarrow v''=8$  emission line profiles in N<sub>2</sub> and D<sub>2</sub> are compared in panels (a) and (b) of Fig. 1. The spectrum in D<sub>2</sub> is blueshifted by  $\sim 55$  cm<sup>-1</sup>

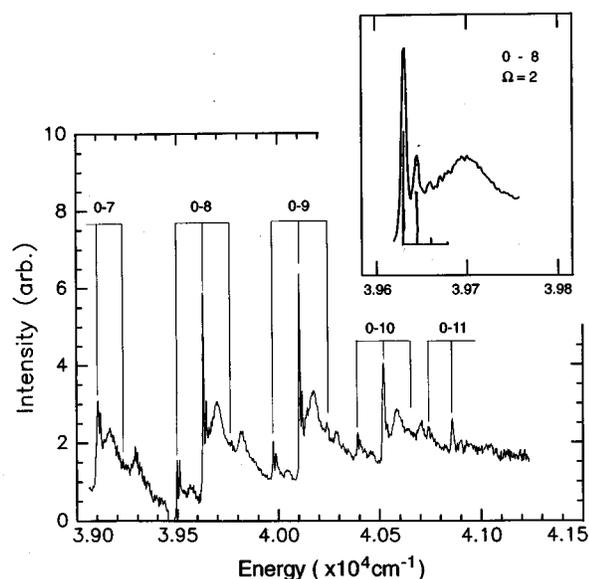


FIG. 2. Excitation spectrum of O<sub>2</sub> isolated in solid D<sub>2</sub>. In the inset an expansion of the  $\Omega=2$  component is shown to illustrate the librational progression. The stick spectrum in the inset represents the calculated Franck-Condon pattern for harmonic oscillations (see the text).

relative to that in N<sub>2</sub>, and the zero-phonon line is significantly broader and shows an extended phonon sideband.

The measured fluorescence lifetimes at 4 K are  $5.4 \pm 0.3$   $\mu$ s and  $216 \pm 15$   $\mu$ s in D<sub>2</sub> and N<sub>2</sub>, respectively. The latter value is in agreement with the earlier measurement of Goodman *et al.*<sup>6(a)</sup> who reported a lifetime of  $234 \pm 10$   $\mu$ s in N<sub>2</sub>, at 4.2 K, and is consistent with the more recent measurements by Kajihara *et al.*<sup>10</sup> Since we do not observe any  $c \rightarrow a$  emission under these conditions, and since the only known non-radiative relaxation channel of  $A'(v=0)$  is via energy transfer to  $c$ , we assume that these lifetimes are determined primarily by radiative relaxation. As already documented in rare gas matrices, these orbitally forbidden transitions are dramatically enhanced. Based on the fluorescence lifetimes, the  $A'$  absorption can be expected to be 50 times stronger in D<sub>2</sub> than in N<sub>2</sub>. Yet, under identical preparation conditions the emission intensities in N<sub>2</sub> are nearly 2 orders of magnitude stronger. Since O<sub>2</sub> and N<sub>2</sub> form ideal solid solutions,<sup>22</sup> it is safe to assume that in dilute N<sub>2</sub> matrices, deposited near 4 K, all O<sub>2</sub> molecules are isolated. Based on the observed emission intensities, and provided that fluorescence quantum yields are near unity in both matrices, we conclude that under the best conditions the observed isolated O<sub>2</sub> concentration is of the order of 1–10 ppm.

Excitation spectra were recorded using a doubled dye laser. A segment of such a spectrum is shown in Fig. 2, and the assigned zero-phonon line origins are collected in Table

TABLE I. Observed zero phonon line positions of O<sub>2</sub>( $A' \leftarrow X$ ) isolated in solid D<sub>2</sub>.

$v$	$\Omega$	$E(\text{cm}^{-1})$			
		Solid D <sub>2</sub>		Gas phase <sup>a</sup>	
2.	3			35 776	
	2	35 809			35 933
1	3		35 956		36 082
	2	36 390		36 505	
3	3		36 690		36 809
	2	36 540		36 662	
7.	3			39 053	
	2	39 105			91 95
1	3		39 237		39 336
	2	39 498		39 574	
8.	3		39 769		39 850
	2	39 630		39 713	
9.	3	39 974		40 036	
	2	40 105		40 171	
1	3		40 240		40 304
	2	40 393		40 432	
10	3		40 642		40 687
	2	40 520		40 560	
1	3	40 740		40 752	
	2	40 860		40 871	
$\Omega=1$		$\Omega=2$	$\Omega=3$	Gas( $\Omega=2$ ) <sup>b</sup>	
$T_e$		34 816(50)	34 679(22)	34 564(46)	34 757
$\omega_e$		795(29)	787(12)	769(22)	812
$\omega_e x_e$		7.3(4.6)	5.8(1.8)	3.0(3)	9.6
$\omega_e y_e$		-0.80(0.2)	-0.87(0.08)	-0.98(0.08)	-0.79

<sup>a</sup>Reference 15.

<sup>b</sup>Reference 13.

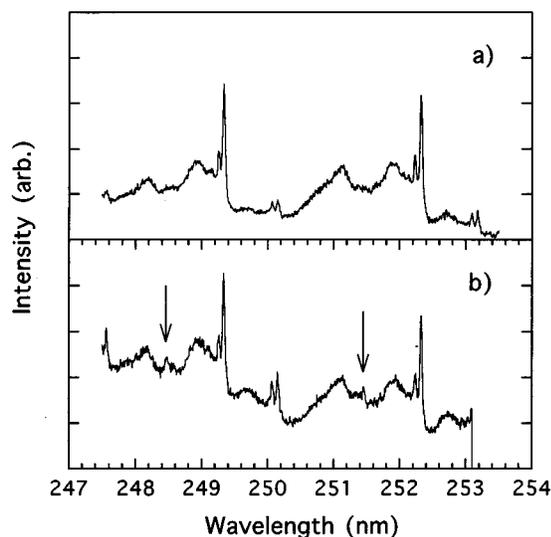


FIG. 3. Excitation spectra in D<sub>2</sub> recorded at (a) 3.6 K; (b) at 7.7 K. Upon warm up the  $\Omega=3$  components become visible (indicated by arrows). The abrupt termination of the spectrum in (b) was due to loss of the sample by evaporation.

I. Here we will adapt the now accepted assignment that the  $^3\Delta$  state is an inverted spin-orbit multiplet,<sup>14</sup> even though as we will argue, our observations are more consistent with a normal triplet. Several aspects are notable about this spectrum. The  $\Omega=2$  components are the strongest transitions. They show a prominent ZPL with a FWHM of  $8\text{ cm}^{-1}$ , followed by a progression of equally sharp but weak sidebands which are regularly spaced with a separation of  $\sim 15\text{ cm}^{-1}$  (see inset in Fig. 2). Although the phonon sidebands of  $\Omega=1$  components are clearly identifiable, the ZPL's are extremely weak, and usually become visible only after annealing at temperatures between 5–7 K. The effect of annealing is shown in Fig. 3. Although weak, the ZPL's of  $\Omega=3$  components show a doublet of almost equal intensity, split by  $\sim 15\text{ cm}^{-1}$ . These features hold throughout the vibrational progression. It can be verified from Table I that the separations between  $\Omega$  components,  $E(\Delta\Omega=1)=A\Lambda\Sigma$ , are equal, within the accuracy of measurement, as would be expected for pure spin-orbit splitting in nonrotating molecules. They decrease monotonically from a spacing of  $2A=150\pm 3\text{ cm}^{-1}$ , for  $v=2$ , to  $133\pm 3\text{ cm}^{-1}$  for  $v=9$ . This vibrational dependence of spin-orbit splitting is nearly identical to that observed in the gas phase.<sup>13,15</sup> In contrast, in both rare gases and in N<sub>2</sub> the splittings are quite erratic.<sup>6</sup> The observed variations in those matrices were ascribed to perturbations due to phonon mediated mixings with the nearby  $A\ ^3\Sigma^+$  state.<sup>6</sup>

To establish whether O<sub>2</sub> rotates in solid D<sub>2</sub> polarization measurements were carried out throughout the  $A'(v=9) \leftarrow X(v=0)$  band. The emission is polarized, with a polarization ratio of  $P \equiv I_{\parallel}/I_{\perp} = 1.25 \pm 0.05$  independent of the excited  $\Omega$  component. Apparently, no rotation of the molecule occurs during its vibrational relaxation from  $v=9$  to  $v=0$ . The polarization ratio is however indicative of a transition dipole perpendicular to the molecular axis both in absorption and emission.

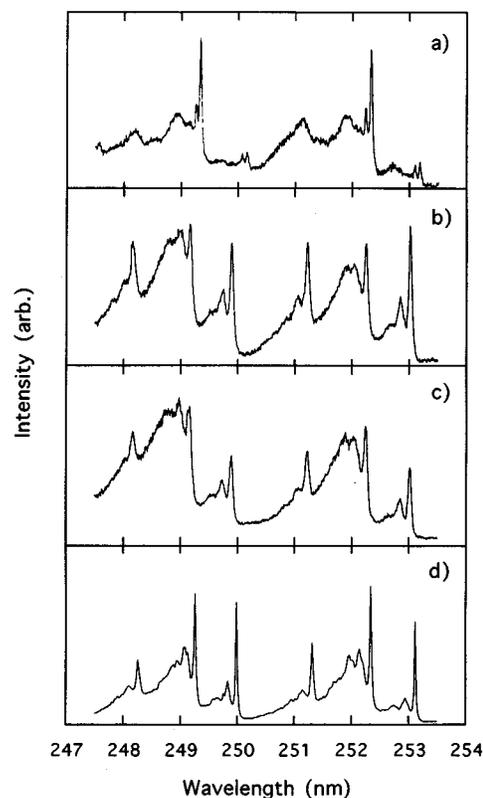


FIG. 4. Excitation spectra of O<sub>2</sub>(A')  $v=8$  and  $v=9$ . (a) in neat D<sub>2</sub> at  $T=3.6\text{ K}$ ; (b) in D<sub>2</sub> overcoated with Xe and after heat cycling up to 27 K (recorded at 7.7 K); (c) in solid H<sub>2</sub> after overcoating with Xe and heat cycling up to 20 K (recorded at 4.1 K); (d) in neat N<sub>2</sub>, recorded at 5.7 K. In all cases, the O<sub>2</sub> concentration in the gas mixture was 0.2%.

In Fig. 4, the  $v'=8-9$  range is shown for monomeric O<sub>2</sub> trapped in different solids: (a) in neat D<sub>2</sub>, (b) in O<sub>2</sub>/D<sub>2</sub> sample overcoated with Xe and after heating it to  $\sim 27\text{ K}$ , (c) in O<sub>2</sub>/H<sub>2</sub> sample overcoated with Xe and after heating it to 20 K, (d) in O<sub>2</sub>:N<sub>2</sub>. Quite clearly the spectra obtained from the overcoated samples resemble that of O<sub>2</sub>/N<sub>2</sub> rather than O<sub>2</sub> isolated in D<sub>2</sub>. The spectra in the overcoated samples survive subsequent heat cycles and show a reversible linear dependence of emission intensity on temperature, such that the emission intensity reduces by  $\sim 50\%$  between 4 and 10 K. It is possible to establish that the perturbations in the overcoated samples are a long-range effect, and not due to O<sub>2</sub> molecules trapped as nearest neighbors to Xe. The  $A' \rightarrow X$  emission is quenched by Xe. This has been well established previously, and we verified it to be true in O<sub>2</sub>/Xe matrices under our experimental conditions. We further test that a single Xe neighbor is sufficient to quench the emission. This is based on measurements in D<sub>2</sub> solids doubly doped with O<sub>2</sub> and Xe, at a concentration of 1:5:500=O<sub>2</sub>:Xe:D<sub>2</sub>. In such solids, the excitation spectra, although weak, are characteristic of O<sub>2</sub> isolated in D<sub>2</sub>, i.e., identical to the spectrum in Fig. 4(a). After recording the excitation spectra, irradiation of these samples at 193 nm produced XeO emission, which is the photodissociation product of O<sub>2</sub>:Xe pairs. Thus we conclude that the emission spectra in the overcoated samples, which can only be obtained after a heat cycle, are from O<sub>2</sub>

molecules which are perturbed by the Xe film, however are coated at least with one full solvation shell of D<sub>2</sub> or H<sub>2</sub>.

#### IV. DISCUSSION

Spectra of O<sub>2</sub> as impurities in solid D<sub>2</sub> and H<sub>2</sub> have been previously obtained by proton beam and electron beam excitation.<sup>17,18</sup> In those samples, prepared from the melt, the oxygen number densities are limited by solubility, which is estimated at  $\sim 1$  ppm. In contrast, binary O<sub>2</sub>/N<sub>2</sub> mixtures make ideal solid solutions with well established phase diagrams.<sup>22</sup> Based on the comparison of LIF intensities between D<sub>2</sub> and N<sub>2</sub>, we conclude that independent of the initial concentration of the gas mixture, under our conditions of preparation, only a very small fraction of the isolated molecules are observable. The monitored emission,  $A' \rightarrow X$ , is known to be quenched in O<sub>2</sub> dimers, and we have verified it to be absent in neat O<sub>2</sub> films. Thus a possible interpretation of the very weak signals in D<sub>2</sub> and its complete absence in H<sub>2</sub> is that extensive segregation occurs during deposition. This is somewhat consistent with the observation that fast deposition leads to enhanced isolation in D<sub>2</sub>, presumably due to reduction of the exposed surface during deposition. Alternatively, as will be argued below, since the spectroscopy under consideration is that of a forbidden transition, it may be strongly site selective and only a minority of the sites may be observable. The prepared samples are quite transparent to the eye, and during thickness measurements some 20–50 He:Ne fringes can easily be observed. Independent of the initial deposition conditions we expect these quantum solids to undergo significant thermal annealing. The phase transitions of D<sub>2</sub> have been well studied.<sup>4,23</sup> In deposited thin films both fcc and hcp structures appear. The phase transition temperature between these two forms depends on the para-D<sub>2</sub> content. The transition is reversible in the case of H<sub>2</sub>, however in the case of D<sub>2</sub> repeated annealing cycles lead to permanent formation of the cubic phase.<sup>23</sup> We expect the bulk of the solid to behave according to this prescription, however, at the isolation site of the guest molecule, the structure may be determined by the O<sub>2</sub>-D<sub>2</sub> interactions. Given the fact that the anisotropy of  $J=1$  states is sufficient to drive the system into the hcp structure, we may expect that the stable trapping sites of O<sub>2</sub> will also be at least locally hcp. Finally, we point out that the experiments are performed in normal D<sub>2</sub>. However, given the fact that O<sub>2</sub> in its ground state is paramagnetic, we expect that its nearest neighbor D<sub>2</sub> molecules are entirely converted to ortho-D<sub>2</sub> within minutes of the deposition. Indeed, the efficient ortho-para conversion of hydrogen by O<sub>2</sub> has recently been used to characterize diffusion in such solids.<sup>20</sup> The above considerations establish a framework for the best initial guess of the description of these samples as O<sub>2</sub> molecules isolated within a cage of ortho-D<sub>2</sub> isolated in a fully equilibrated crystallite of normal D<sub>2</sub>.

##### A. The solvated potential

In Table I, we list the observed O<sub>2</sub> ZPL energies in solid D<sub>2</sub>, along with the gas phase values. Similar to the gas phase data, the vibrational progressions in the excited state can be fitted satisfactorily only if cubic anharmonicity terms,  $\omega_e y_e$ , are included. The electronic origin in solid D<sub>2</sub> has undergone

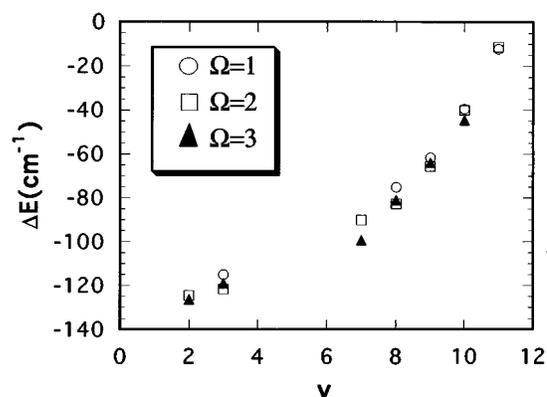


FIG. 5. Matrix shift as a function of vibrational quantum number. The ordinate is the difference between gas phase and solid state energies,  $E_g - E_s$ , plotted versus the vibrational quantum numbers. The redshift of  $\sim 120$  cm<sup>-1</sup> at  $v=0$ , reduces to zero at the dissociation limit.

a red shift of  $\sim 100$  cm<sup>-1</sup>. The harmonic frequencies are lowered by  $\sim 3\%$ . The potential is more harmonic in the solid state ( $\omega_e x_e$  is reduced) while the cubic anharmonicities are almost identical to that of the gas phase. There is significant uncertainty in these values as indicated by the error bars on the derived parameters. The most reliable values are those derived from the progression in the  $\Omega=2$  component. In spite of the uncertainties in the derived parameters indicated by the error limits, there clearly are systematic differences between the gas phase and the solvated potential. This can be discerned from a comparison between energies of observed lines, shown in Fig. 5. The trend in this comparison is quite obvious. While the electronic origin, and the  $v=0$  level, are red shifted by  $\sim 120$  cm<sup>-1</sup>, the effect is completely counter balanced by repulsion in the O(<sup>3</sup>P)+O(<sup>3</sup>P) limit. It is important to note that the zero-shift limit is not reached asymptotically. Extrapolation of the curve would lead to positive shifts, creating states bound by the repulsive cage potential above the dissociation limit of the free molecule. Indeed, 193 nm excitation of the molecule does not lead to dissociation. Instead, we observe fluorescence from  $A'(v=0)$ . Thus solid D<sub>2</sub> is effective in caging the O(<sup>3</sup>P) photofragments. Nevertheless, the molecular dissociation limit, within a few wave numbers, is unchanged.

If one assumes that the X state is well represented by the gas phase parameters, then the vibrational analysis establishes uniquely that the emission originates from the lowest  $\Omega$  level of the multiplet. The interconversion between different  $\Omega$  states, via nonradiative energy transfer, is thus efficient in the matrix, as would be expected for light molecules with relatively small spin-orbit splitting. The extended red shoulder observed in emission, in Fig. 1, is then to be assigned to an extended phonon sideband.

##### B. The isolation site

In what follows we first attempt a consistent explanation of the observations: that only two of the  $\Omega$  components show prominent ZPL's in excitation; that the overall transition di-

pole between  $A'$  and  $X$  is strongly enhanced in D<sub>2</sub> and that this transition dipole is perpendicular to the molecular axis.

O<sub>2</sub> belongs to Hund's case (a), where  $\Lambda$  is well defined. Since the ground state is  $\Sigma$ , the polarization indicates that the transition dipole is perpendicular to the molecular axis, indicative of a  $\Delta\Lambda = \pm 1$  transition. The ground state is well isolated from other electronic states with which it may interact, and it is known to be essentially unperturbed in matrices. The upper state must therefore have  $\Pi$  character, i.e., the transition must gain its intensity by mixing the upper  ${}^3\Delta_u$  state with a  $\Pi$  state which in turn is strongly coupled radiatively to the ground state. Since spin and parity selection rules are preserved, this state must be a triplet with  $u$  parity. The nearby repulsive  ${}^3\Pi_u$  state, which is radiatively coupled to the ground state, and which has also been shown to be mixed with the  $A'$  state in the free molecule, in the gas phase,<sup>14</sup> can therefore be identified as the origin of intensity borrowing. This is also consistent with the fact that both the spacings and intensities of the  $\Omega$  states remain regular throughout the  $A'$  vibrational manifold.

Having established the state which is mixed with the  ${}^3\Delta_u$ , we consider mechanisms of intensity borrowing to interpret the observed  $\Omega$  components. Since in the matrix the molecule does not rotate, in the case of ZPL's, the only  $\Omega$  specific mechanism for interaction between  ${}^3\Delta_u$  and  ${}^3\Pi_u$  states is via spin-orbit coupling. In first order perturbation, spin-orbit coupling can only mix the  ${}^3\Delta_1$  and  ${}^3\Delta_2$  components with the  ${}^3\Pi_1$  and  ${}^3\Pi_2$ , respectively.<sup>24</sup> The  ${}^3\Delta_3$  component will only mix via spin-rotation coupling, which clearly cannot occur in a nonrotating state. Thus we would not expect to be able to observe the ZPL of the  $\Omega=3$  component. This would suggest the assignment of the lower energy ZPL to  $\Omega=1$ , and the higher energy component for which only the phonon sideband can be observed to  $\Omega=3$ . This would imply that *the spin-orbit multiplet in the  ${}^3\Delta$  state is normal*, in agreement with the initial assignment by Herzberg,<sup>11</sup> and in conflict with the more recent analyses of the gas phase  $A' \rightarrow X$  transition.<sup>12-16</sup> Note, the fact that the phonon sidebands of all three  $\Omega$  components are visible does not contradict this interpretation. Under the phonon sidebands, the molecule undergoes significant librational motion, a degree of freedom which can be regarded as a rotational superposition state, since it can be expanded in a rotational basis.<sup>25</sup> The rotational superposition in turn implies the possibility of intensity borrowing via spin rotation, which couples all three  $\Omega$  components of the  ${}^3\Delta$  state with the  ${}^3\Pi$  state.<sup>24</sup> These mixings, as stated, are already present in the gas phase molecule, and given the light mass of the host atoms, we do not expect additional spin-orbit mixings induced by the host.

While the observed lines can be rationalized, the strong enhancement of the radiative lifetime needs to be explained. In the absence of external heavy atom effects, the lattice perturbations are electrostatic in nature. This implies mixing of orbitals only. Remembering that the transition dipole is perpendicular to the molecular axis, we require an interaction potential that can mix  $\Delta$  and  $\Pi$  orbitals

$$V_{\text{int}} = \langle S\Sigma | \langle L\Lambda | V(R, \theta, \phi) | L'\Lambda' \rangle | S\Sigma' \rangle \\ = \langle L\Lambda | V(R, \theta, \phi) | L'\Lambda' \rangle \delta_{SS'} \delta_{\Sigma\Sigma'}. \quad (1)$$

The interaction potential should be possible to expand in terms of spherical harmonics centered on the isolation site

$$V(R, \theta, \phi) = \sum_{kl} V_{kl}(R) Y_{kl}(\theta, \phi). \quad (2)$$

Noting that for the  $\Pi$  state,  $L=2$  and  $\Lambda = \pm 1$ ; and for the  $\Delta$  state,  $L'=2$  and  $\Lambda' = \pm 2$ , and based on the algebraic closure  $l = \Lambda + \Lambda'$ ; the only acceptable values of  $l$  are 1 and 3. Based on the vector relation  $k \geq L + L'$ ,  $k \geq 4$  is required. In addition, we require that  $V_{\text{int}}$  transform according to the totally symmetric representation of the lattice site. In hcp lattices, the requirement of invariance with respect to reflection of  $z \rightarrow -z$ , precludes odd  $l$  values. Therefore the required mixing cannot occur in hcp sites. The site symmetry in fcc lattices is octahedral. The anisotropic part of the totally symmetric representation in  $O_h$ , with the  $z$  axis (molecular axis) pointing along  $[100]$ , is given as  $Y_{44} + Y_{4-4}$ .<sup>26,27</sup> This also fails to produce the required mixing. However, for the  $z$  axis aligned along the  $[111]$  direction, the potential in an octahedral site is given as<sup>27</sup>

$$V(R, \theta, \phi) = V(R) \{ Y_{40} - (10/7)^{1/2} [-Y_{43} + Y_{4-3}] \}. \quad (3)$$

The anisotropic part of this potential,  $[-Y_{43} + Y_{4-3}]$  has the requirements set above for mixing the  $\Pi$  and  $\Delta$  states. Moreover, there are no other sites in cubic or hexagonal solids that provide such site symmetry. We conclude that the observed molecules are those that are isolated in sites with equilibrium fcc structure, and which point along the  $[111]$  direction.

The unique site requirement for the enhanced oscillator strength of the transition presents an alternative explanation for the very small number density of observable molecules in D<sub>2</sub>. If the majority of the molecules were isolated in hcp sites, and in such sites the transition oscillator were comparable to that of the free molecule ( $\tau_{\text{rad}} = 10-50$  s), then they would be essentially invisible in comparison with the molecules that fluoresce with a radiative lifetime of  $\sim 5$   $\mu\text{s}$ . This interpretation also provides a rationale for the observations in the overcoating experiments. As described in the results section, upon deposition of O<sub>2</sub>:H<sub>2</sub> samples, initially we fail to observe any LIF from O<sub>2</sub>. However, after overcoating with Xe and heat cycling, isolated O<sub>2</sub> molecules become observable. This suggests that isolated O<sub>2</sub> molecules were present in H<sub>2</sub> prior to the treatment, and that they only become observable as a result of perturbation by the Xe overlayer. We propose that in bulk H<sub>2</sub>, the O<sub>2</sub> impurity drives the local structure into hcp. In the presence of the Xe overlayer, pockets large enough to contain O<sub>2</sub> fully solvated by H<sub>2</sub> form, but with an fcc local structure due to the proximity of the fcc Xe overlayer. As mentioned previously O<sub>2</sub> molecules in contact with Xe do not emit. Note also, that similar experimental observations were made in D<sub>2</sub>. Upon overcoating and heat cycling, the spectra perturbed by Xe develop and overwhelm the spectrum of the molecule isolated in D<sub>2</sub>.

While the above considerations give a consistent interpretation of the observations in D<sub>2</sub>, the perturbations are significantly more complicated in the heavier rare gases, in N<sub>2</sub>,

and in the overcoated samples. The more difficult observation to rationalize is that of the prominence of both  $\Omega=1$  and  $\Omega=3$  components which appear with nearly equal intensity in the heavier solids (this statement is independent of the assignment of the order in the multiplet). In both N<sub>2</sub> and Ar, a polarization of 1.3 is observed, as in the present case, and therefore spin-rotation coupling cannot be invoked. On purely electrostatic grounds, to first order in perturbations, we cannot rationalize the prominence of the  $\Omega=3$  component. It is necessary to invoke the external heavy atom effect, i.e. exchange forces, as a means of transferring spin-orbit coupling to the molecule from the host. The vibration specific perturbations of the different  $\Omega$  components in the heavier van der Waals crystals, which have been described in some detail, are further indication of strong perturbations in the nested manifold of electronic states which are absent both in the free molecule and in molecules isolated in D<sub>2</sub>. The same arguments need to be invoked to explain the prominent ZPL's in the samples that were annealed after being overcoated with Xe.

### C. Librational dynamics:

The splittings of the  $\Omega=1$  ZPL's, and the progression built on the  $\Omega=2$  component, show the same spacings, and would therefore appear to have the same origin. There are in principle two possible sources of this structure: libration, or center of mass motion (a local phonon). We favor the former. Given the mass asymmetry between the cage atoms and the impurity, center of mass motion would mainly involve the D<sub>2</sub> molecules and would be expected to produce a variety of frequencies associated with the normal modes that arise from the 12-fold coordination. As such, a single progression would not be expected from such motions.

The earliest treatment of hindered rotations of a diatomic in a field of octahedral symmetry is due to Devonshire.<sup>25</sup> Based on his tabulation, or the more extensive tabulations by Sauer,<sup>28</sup> it is possible to assign barrier heights to rotations of most diatomics substitutionally isolated in octahedral sites. The in the case of the <sup>3</sup> $\Delta$  state, it is more appropriate to consider the hindered rotations in a symmetric top basis set. However, in the case of free spinning around the molecular axis (preserved  $\Lambda$  and  $\Omega$  in the present), the treatment of the hindered rotations are nearly identical to that of the diatomic.<sup>29</sup> These models should be used with caution in the case of a heavy impurity isolated in a light host, since correlations between molecular and cage motion are to be expected. Thus if we assume the librator to have the moment of inertia of bare O<sub>2</sub>,  $B=0.75$  cm<sup>-1</sup> for  $v=7$  in the <sup>3</sup> $\Delta$  state,<sup>16</sup> then the observed uniform spacings of 15 cm<sup>-1</sup> ( $\sim 20 B$ ) in the progression built on the  $\Omega=2$  component would imply that the motion is already in the harmonic oscillation limit, and a potential barrier to end-over-end rotation of  $\sim 50 B$  ( $\sim 40$  cm<sup>-1</sup>) can be estimated. In the harmonic limit, analysis of librations in rotational basis sets is unnatural. Instead, we consider a one dimensional angular oscillator:

$$-\frac{\hbar^2}{2I} \frac{\partial^2 \varphi}{\partial \theta^2} + \frac{1}{2} k(\theta - \theta_e)^2 = E \varphi \quad (4)$$

for which  $\omega = (k/I)^{1/2}$ . Note, for identical force constants in the excited and ground states we expect  $\omega_e''/\omega_e' = (B''/B')^{1/2} \sim 1.4$ . Thus based on the spacings in the excited state progression of 15 cm<sup>-1</sup>, a ground state librational frequency of  $\sim 21$  cm<sup>-1</sup> would be expected. This is in good agreement with the observed satellite peak in emission which is separated from the ZPL by  $\sim 25$  cm<sup>-1</sup>. Using the experimentally determined oscillation frequencies,  $\omega_e'' = 25$  cm<sup>-1</sup> and  $\omega_e' = 15$  cm<sup>-1</sup>, the harmonic angular wavefunctions were calculated and the Franck-Condon factors were computed as a function of separation between potential minima  $\theta_e$ . The observed intensity patterns of the observed splittings can be produced for  $|\theta_e' - \theta_e''| = 17^\circ$  and  $26^\circ$ , for the  $\Omega=2$  and  $\Omega=1$  components, respectively. These stick spectra are shown in Fig. 2. The harmonic nature of the observed progression suggests that indeed the effective moment of inertia of the molecule in the solid is significantly larger than in the bare molecule, implying correlation between the motions of the immediate cage and the molecular oscillations. The assumption of effective moments of inertia larger than those of the bare molecule in Eq. (4) would simply lead to the prediction of smaller tilt angles between excited and ground states. Independent of the exact values used in this model, a relative tilt of the molecular axis is required to produce the observed intensity patterns in the progressions. Such a tilt could in principle result from a partial decoupling of the electronic angular momentum from the molecular axis, presumably, by coupling to the crystal field axis.

### V. CONCLUSIONS

The O<sub>2</sub>(A'-X) transition has been observed and analyzed in solid D<sub>2</sub>, yielding a detailed description of the structure and motions of the guest and its environment. Due to the orbitally forbidden nature of this transition, and its enhanced oscillator strength in van der Waals solids, the transition is a sensitive probe of local interactions. It is concluded that only molecules isolated in fcc sites, and aligned along the crystal [111] direction, are being observed in solid D<sub>2</sub>. Whereby, the absence of the spectrum in solid H<sub>2</sub> is ascribed to trapping in hcp sites there. The same rationale leads us to speculate that in samples overcoated with Xe and subjected to thermal annealing, O<sub>2</sub> isolated in fcc H<sub>2</sub> is formed in pockets of the Xe overlayer.

The observed isolated monomers in solid D<sub>2</sub> are subject to a large rotational barrier, and undergo nearly harmonic oscillations along with the immediate cage atoms. This is to be contrasted with recent studies in heavy rare gases in which free rotations of CN have been shown.<sup>30</sup> In solids such as Xe a substitutional cavity does not "collapse," due to the repulsions between cage atoms. Thus a small substitutional impurity will be in a nearly isotropic, loose cavity, hence free to rotate. In quantum solids, due to the large zero-point amplitudes, the cage atoms will collapse around the impurity to minimize the total energy. This leads to a picture of a tight O<sub>2</sub>(o-D<sub>2</sub>)<sub>12</sub> cluster isolated in the normal D<sub>2</sub> host. The same picture is reached in studies in overcoated samples. After heat-cycling these solids, isolated molecular spectra are observed, which although perturbed by the Xe film, are shown

to be surrounded by at least one complete shell of hydrogen molecules. In effect, when the guest–host potentials are deeper than the host–host potentials, the first solvation shell will be strongly localized radially. If the radial guest–host potential contains a minimum significantly deeper than the H<sub>2</sub>–H<sub>2</sub> pair potential, then the first solvation shell will be localized, losing its quantum character at least along the radial coordinate. This picture has been used to account for the stable cryogenic condensates of discharged N<sub>2</sub>/He where large number densities of N atoms are observed.<sup>31</sup>

The spectra in the overcoated samples, which closely resemble those in heavier van der Waals lattices, are less well understood. However, the prominence of  $\Omega=3$  transitions in such solids may be taken as indication that exchange interactions play a significant role in perturbing the molecular states in heavier solids.

Our analysis of the spin–orbit multiplet in the A' state leads us to believe that the spin–orbit splitting is normal. The ordering of the  $\Omega$  states cannot be altered by the lattice, the same should be true of the gas phase molecule, in contradiction with the presently accepted assignment.

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