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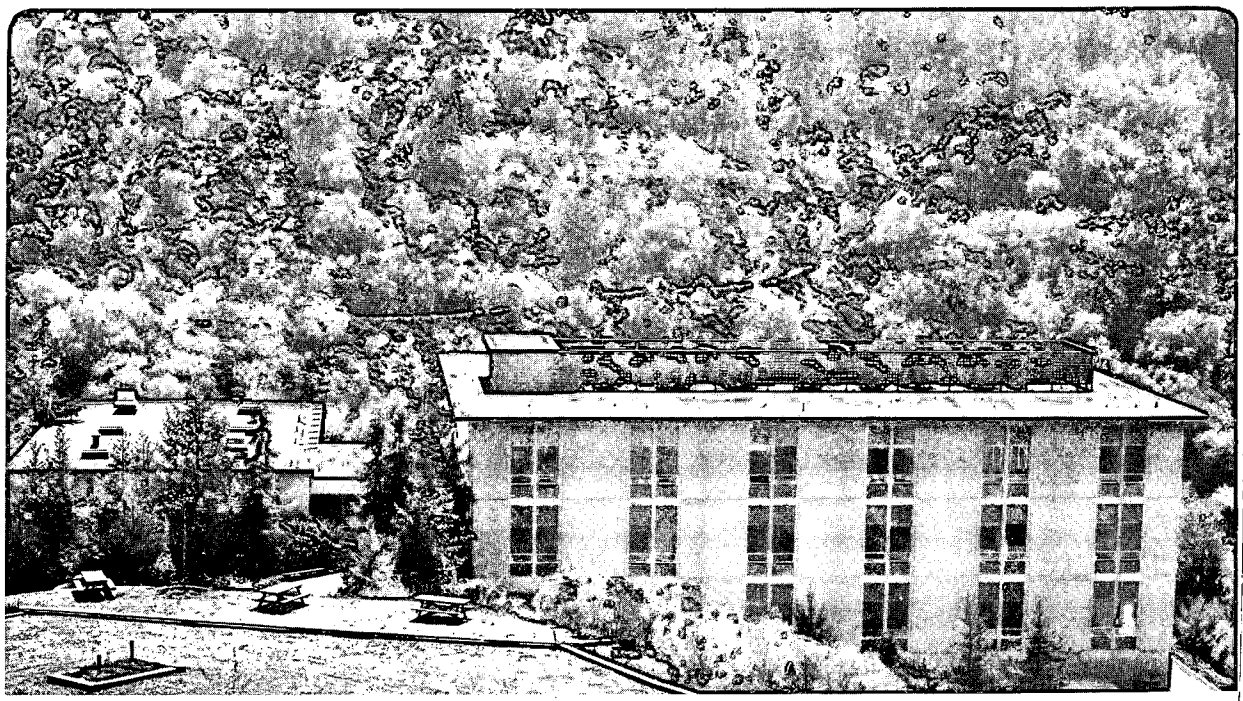
October 1993



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MAGNETIC, OPTICAL AND CHARGE-TRANSFER SPECTRA OF ANTIFERROMAGNETIC SOLID α - O_2 AND "PARAMAGNETIC" SOLID β - O_2: A SMALL-CLUSTER, MANY-ELECTRON CALCULATION*

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Magnetic, Optical and Charge-Transfer Spectra of Antiferromagnetic Solid $\alpha - O_2$ and "Paramagnetic" Solid $\beta - O_2$: A Small-Cluster, Many-Electron Calculation.

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Abstract

The electronic spectra of α and β solid O_2 were calculated in a full many-body approach for a cluster consisting of four O_2 molecules with periodic boundary conditions. By including only the partially occupied π orbitals (16 spin-orbitals, 8 electrons) the basis set consists of 12870 many-electron states. Use of the symmetry properties (group-theoretical analysis) simplifies the problem considerably. Resulting spectra – with phenomenological Hamiltonian parameters obtained from experiment – consist of separate regions: (a) 81 states corresponding to the ground state and low-energy magnetic excitations (magnons); (b) 1215 states of neutral molecular excitations (excitons); and (c) 11574 charge-transfer states (conducting high-energy states). Analysis of the properties of the ground states in both α and β solid O_2 has been carried out.

I. INTRODUCTION

The open-shell character of the O_2 molecule makes solid O_2 a molecular crystal with a very rich structure. The two lowest-temperature phases of solid molecular oxygen[1–3] have interesting properties: they are insulating, exhibit complicated magnetic behavior[1,4–8] and their optical properties[9–12] resemble gaseous molecular oxygen in their gross features, but present peculiar properties of their own, such as side bands and Frenkel excitons.

Band theory yields for both phases a half-filled band derived from the $2p$-π antibonding orbitals, i.e., a metal, even though experimentally they are both insulators. Solid O_2 is therefore a prototypical Mott insulator[13]. The monoclinic α phase and the rhombohedral β phase are orientationally ordered. The molecules are packed in layers with their axes perpendicular to the layer planes (the $a-b$ planes, see Fig. 2 of Ref.5). In the β phase these layers form a hexagonal lattice, whereas in the α phase – where the layers have center-rectangular symmetry – the hexagons are slightly distorted. Monoclinic $\alpha - O_2$ is the only elemental solid that is known to be both insulating and antiferromagnetic. It is known that all spins are aligned along the monoclinic axis $\pm\mathbf{b}$, with all nearest neighbors in an antiparallel arrangement to each other.

The β phase, with triangular arrangement of the molecules in each plane – three fully symmetric sublattices but never two – cannot be a classical antiferromagnet: frustration prevents all nearest neighbors to align themselves in an antiparallel configuration. The β phase has been variously described[5,8] as either paramagnetic, or antiferromagnetic with strong but only short-range order.

From the discussion above it can be seen that any theoretical treatment of molecular solid O_2 requires the inclusion of the strong electron-electron correlations from the beginning, and not as a perturbation or an afterthought. In the present work, an exact diagonalization of the many-electron Hamiltonian for a small cluster of four O_2 molecules is performed. The molecules are in a planar arrangement (the $a-b$ plane) with periodic boundary conditions. The use of the periodic-small-cluster approximation in treating strong correlated materials

is well established[14]. Solid O_2 can be viewed as a set of weakly interacting molecules with strong intra-molecular correlations. The dominant interactions, therefore, are short range. This fact makes it an ideal candidate for the small-cluster method.

Section II presents the Hamiltonian. The results are discussed in section III, followed by the conclusions.

II. THE HAMILTONIAN

Consider a set of mutually orthogonal Löwdin spin orbitals of the O_2 molecule, two of each spin on each molecule. When the molecules are far apart these are the real x and y orbitals corresponding to π_g^- symmetry and derived from the atomic-oxygen $2p$ states. Attached to them there are creation (destruction) operators $c^\dagger_{i,\mu,\sigma}$ ($c_{i,\mu,\sigma}$), where i stands for the molecular site (location of the O_2 molecule), μ for the spatial orbital (π_x or π_y) and σ for the spin ($\uparrow$ or $\downarrow$). The Hamiltonian for the system contains one- and two-particle terms:

$$H = \sum_{i,j}\sum_{\mu,\nu}\sum_{\sigma} t^{\mu,\nu}_{i,j} c^\dagger_{i,\mu,\sigma} c_{j,\nu,\sigma} + \frac{1}{2}\sum_{i,j,k,l}\sum_{\mu,\nu,\epsilon,\lambda}\sum_{\sigma,\sigma'} U^{\mu,\nu,\epsilon,\lambda}_{i,j,k,l} c^\dagger_{i,\mu,\sigma} c^\dagger_{j,\nu,\sigma'} c_{k,\epsilon,\sigma'} c_{l,\lambda,\sigma} \tag{1}$$

where $t^{\mu,\nu}_{i,j}$ and $U^{\mu,\nu,\epsilon,\lambda}_{i,j,k,l}$ are the one- and two-particle matrix elements. This Hamiltonian can be further rewritten as[12]

$$H = \sum_i H_i + H_{int} \tag{2}$$

where $\sum_i H_i$ is the Hamiltonian of infinitely separated, non-interacting molecules, and H_{int} accounts for those contributions involving more than one molecule at a time. The Hamiltonian for one single O_2 molecule, H_i, is fully written in Ref. 12 [equation (3.1)]. The same set of single-molecule parameters quoted there has been used in the present calculation.

Even though the H_{int} Hamiltonian contains both interactions – including crystal fields – and electron-hopping terms, only those terms which involve electron transfer between molecules are kept in this calculation. They are, by far, the dominant contribution since they involve two-molecule, one-electron energies[12]. In addition, if three- and four-center integrals

are neglected, all inter-molecular contributions can be written in terms of two parameters, V_ξ and V_η, which correspond to hopping integrals between Löwdin orbitals centered on two neighboring molecules. The molecules have their own axes always perpendicular to the line joining the two molecular centers, and the orbitals are all π antibonding. For V_ξ the π-orbitals are oriented along the inter-molecular axis [they yield (π-π)-σ four-center orbitals]. For V_η the π-orbitals are oriented in the direction perpendicular to the inter-molecular axis [they yield (π-π)-π four-center orbitals].

The interaction V_η is much smaller than V_ξ and was also neglected,

$$V_\eta = 0 \quad ;$$

V_ξ was determined by fitting the low-energy magnetic excitations for the $\alpha - O_2$ phase. With the experimental[7] value $J = 4.88$ meV of the phenomenological Heisenberg interaction, the best fit was $V_\xi = 0.16$ eV. This value is for an inter-molecular separation of $R = 3.20\mathring{A}$, equal to the distance between nearest neighbors in $\alpha - O_2$. For other neighbors – both in α and β oxygen – an R-dependence $V_\xi \propto R^{-5}$ has been assumed[7]. This dependence yields $V_\xi = 0.11$ eV for the second neighbors in $\alpha - O_2$ and $V_\xi = 0.14$ eV for the nearest neighbors in $\beta - O_2$.

The Hamiltonian was exactly diagonalized, numerically, for the values of parameters discussed above, and with the use of group-theoretical techniques that take fully into account space and spin symmetries. The largest matrix to be diagonalized was 592×592. The resulting spectra are discussed below.

III. RESULTS

For each of the solid phases (α and $\beta - O_2$) considered in this work, there are 12870 many-electron basis functions. Of these, 81 states correspond to all O_2 molecules in their neutral ground electronic state ($^3\Sigma_g^-$). They include the ground state(s) of the many-molecule system and all the magnetic excitations (spin waves, i.e., various relative orientations of

the molecular spins). There are additional 1215 states that correspond to all neutral O_2 molecules, but with at least one molecule in an excited state, either $(^1\Delta_g)$ or $(^1\Sigma_g^+)$ (solid-state molecular Frenkel excitons). Finally, 11655 states exhibit one or more units of electron-charge transfer. The results are shown in Figs. 1 through 6. Figures 1 and 4 show the full spectra of α and β oxygen, respectively. Both spectra are similar, with large gaps separating regions of non-zero density of states. Each band of states is associated with different number of electrons transferred between molecules.

Figures 2 and 5 show amplified views of the 1296 lowest states of α and β oxygen, respectively. There is no charge transfer between O_2 molecules for these states. Again, the overall shape of the spectrum is very similar for the two phases of oxygen, the main difference being a density of states that peaks at a lower energy for $\beta - O_2$. These states include optical excitations of a single molecule, as well as simultaneous excitations of various molecules.

Figures 3 and 6 show the 81 lowest states for α and $\beta - O_2$, respectively. These are the states associated only with magnetic excitations. As expected, the two spectra are very different in this energy range, reflecting the dissimilar magnetic properties observed in α and β oxygen. Both phases possess a singlet ground-state, but whereas in $\alpha - O_2$ it is non-degenerate, in $\beta - O_2$ it has a space-group induced two-fold degeneracy. Moreover, the magnetic excitation spectra are strikingly different. In $\alpha - O_2$ the 81 states are spread over a broad range (maximum excitation energy of 86 meV); in contraposition the magnetic excitation spectrum of $\beta - O_2$ is narrower (maximum excitation energy of 66 meV), and the states, because of the hexagonal symmetry, are highly degenerate.

IV. CONCLUSIONS

The $\alpha - O_2$ and $\beta - O_2$ molecular solids were studied in the periodic small-cluster approximation. The Hamiltonian included all the intra-molecular correlations necessary to describe well the oxygen molecular spectra plus an electron-hopping interaction between the

molecules. The main conclusions from this calculation are:

(1) Solid $\alpha - O_2$ and solid $\beta - O_2$ can be well described in the first approximation by a collection of very weakly interacting O_2 molecules. The spectra, except in the low-energy range, are very similar to the spectrum of neutral and ionized O_2 molecules.

(2) In the O_2 molecule there are exactly $n = 2$ electrons in the antibonding π-orbitals, with no number fluctuations, i.e., $(\delta n/n)_{molecule} = 0$. In the solids, because of the inter-molecular hopping there is a fluctuation in the number of electrons in the π-orbitals; it is, however, very small: $(\delta n/n)_{\alpha-oxygen} = 0.030$ and $(\delta n/n)_{\beta-oxygen} = 0.026$.

(3) In solid $\alpha - O_2$, because of the monoclinic symmetry, there is an anisotropy in the occupation of the x-like and y-like π-orbitals; this asymmetry is also very small, of the order of 2×10^{-5} electrons.

(4) The magnetic excitations in solid $\alpha - O_2$ and in solid $\beta - O_2$ can be well described by a Heisenberg-like Hamiltonian. For the values of parameters used in this work, the best fit for the exchange interactions is: $J = 4.3$ meV for the $\alpha - O_2$ four nearest neighbors; $J = 2.2$ meV for the $\alpha - O_2$ two second neighbors; and $J = 3.3$ meV for the $\beta - O_2$ six nearest neighbors. The interaction arises from virtual hopping of electrons to neighboring molecules; these values agree well with second-order perturbation calculations[12].

(5) Solid $\beta - O_2$ is not a paramagnet, but rather a frustrated triangular-lattice antiferromagnet, with very strong spin correlations between neighboring O_2 molecules: its excitation spectrum is extremely well described by a Heisenberg Hamiltonian with nearest-neighbor-only interactions.

(6) Although the ground states in both solid phases are spin singlets, the ground state of $\beta - O_2$ is, because of the frustration caused by the triangular-lattice symmetry, degenerate.

(7) The magnon spectra of the two phases of solid oxygen differ considerably. The spin-wave excitation spectrum of $\alpha - O_2$ extends to 86 meV, has a mean energy of 43.1 meV and a standard deviation of 21.3 meV. On the other hand the spin-wave excitation spectrum of $\beta - O_2$ extends to 66 meV, has a mean energy of 26.6 meV and a standard deviation of 18.8 meV. In other words, the magnetic excitations of the trigonal β phase are less energetic,

and less dispersed than in the α phase. Entropy considerations clearly point out that these magnetic excitations should be extremely important – in fact be the driving mechanism – for the α-to-β first-order transition observed at $T = 23.9\ K$. If the transition were exclusively caused by magnetic (electronic) excitations – and lattice-vibration contributions, which are much smaller, were neglected – the present calculation would yield a difference in internal energies per molecule, at the transition temperature, between the higher-energy β' and the lower-energy α phases of $\Delta U = 0.9\ meV/molecule$, corresponding to the calculated values of $T\ \Delta S$ at $T = 23.9\ K$.

ACKNOWLEDGMENTS

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FIGURES

FIG. 1. Spectrum of $\alpha - O_2$ including all 12870 states. The numbers above each region of the spectrum indicate the total number of states contained in that region. All states, with the exception of the lowest 1296, are electron-charge-transfer states.

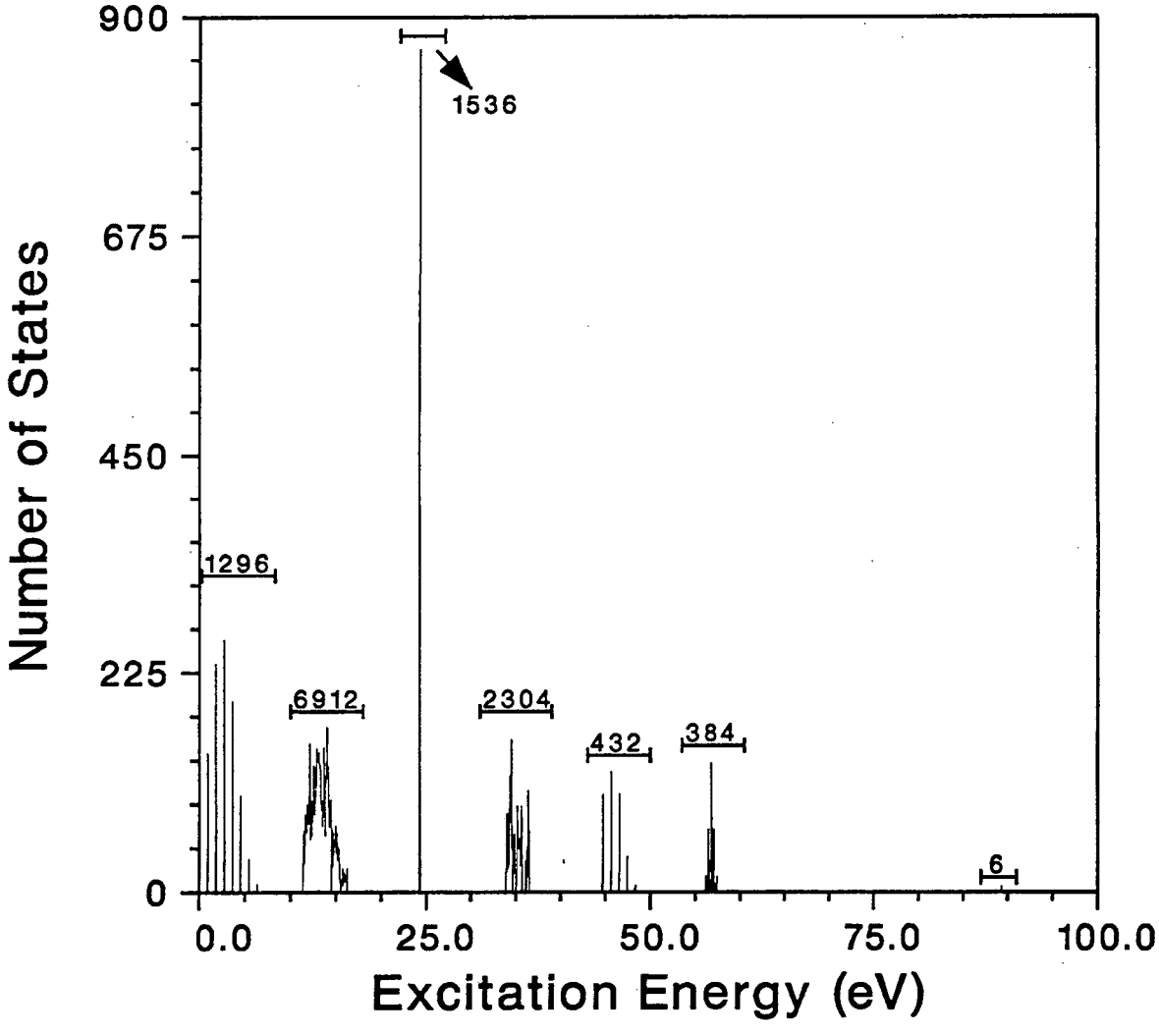
FIG. 2. Spectrum for the lowest 1296 (neutral) states of $\alpha - O_2$. The numbers above each band (magnetic excitations and Frenkel excitons) indicate the total number of states contained in that band.

FIG. 3. Lowest 81 states (magnetic excitations) of $\alpha - O_2$. The single, non-degenerate ground-state is indicated by a circle at zero excitation energy.

FIG. 4. Spectrum of $\beta - O_2$ including all 12870 states. The numbers above each region of the spectrum indicate the total number of states contained in that region. All states, with the exception of the lowest 1296, are electron-charge-transfer states.

FIG. 5. Spectrum of the lowest 1296 (neutral) states of $\beta - O_2$. The numbers above each band (magnetic excitations and Frenkel excitons) indicate the total number of states contained in that band.

FIG. 6. Lowest 81 states (magnetic excitations) of $\beta - O_2$. Note that the ground state is doubly degenerate – circle for two states at zero excitation energy – and that there is a singlet excited state at very low energies: 0.78 meV.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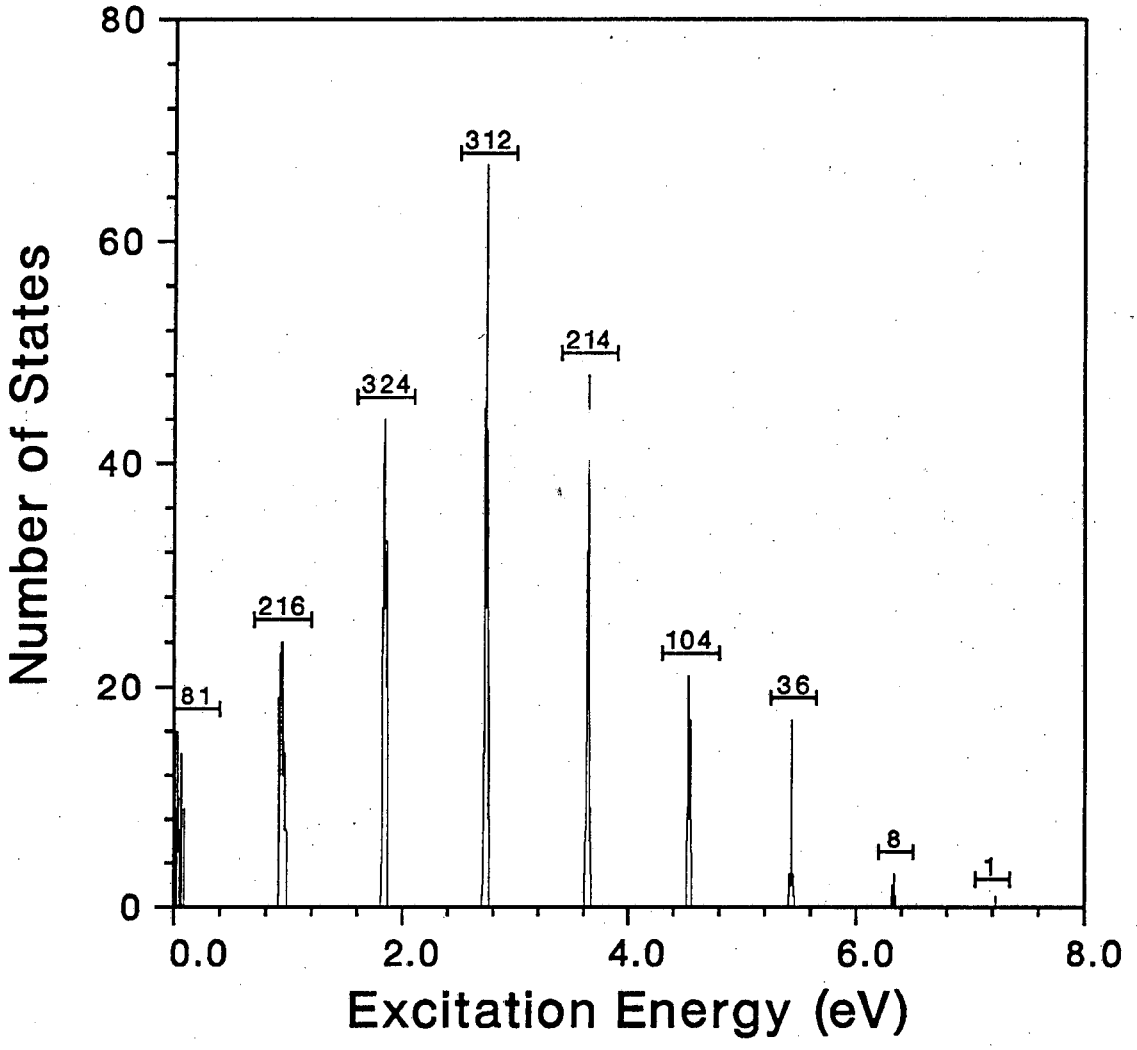
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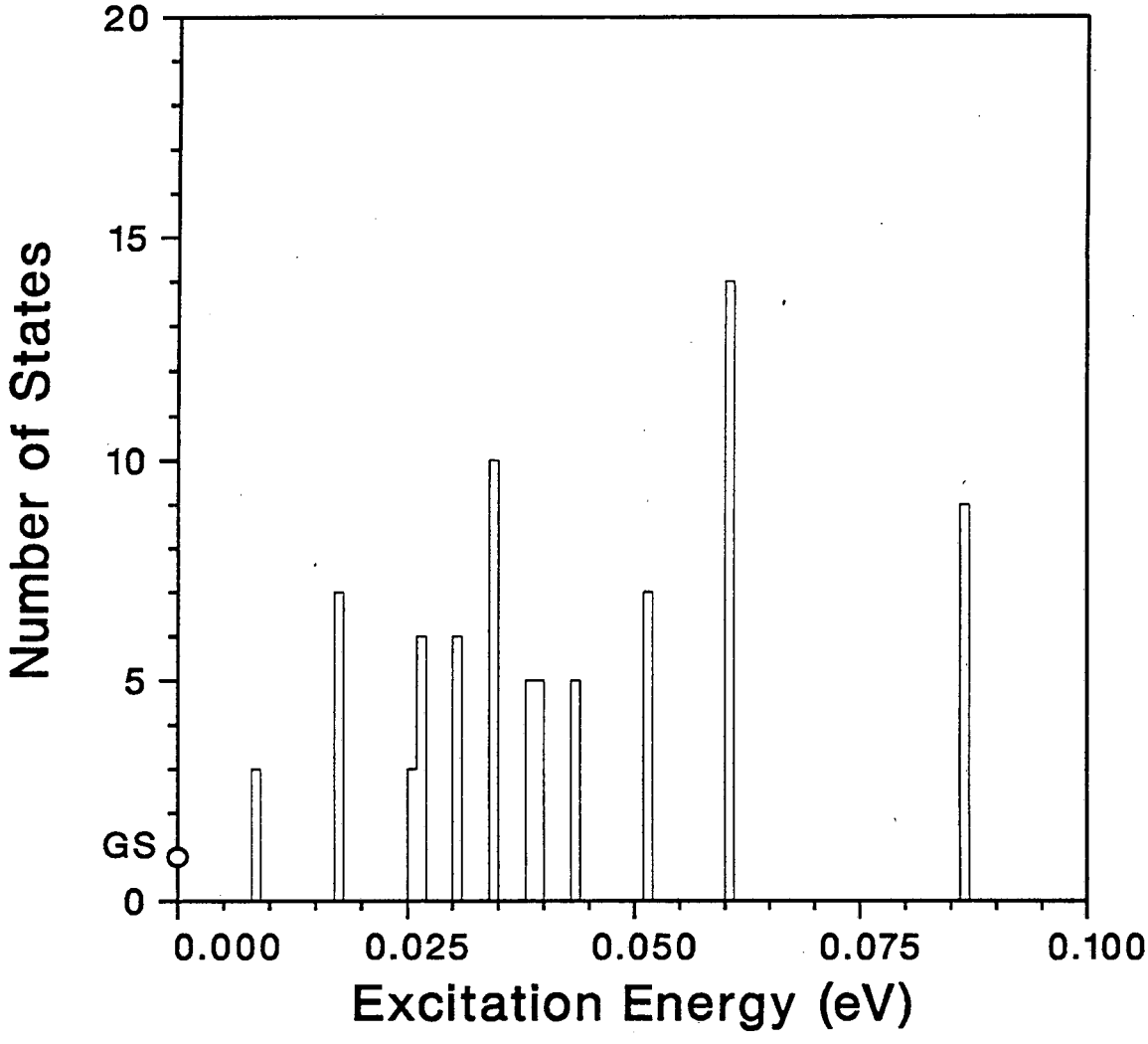
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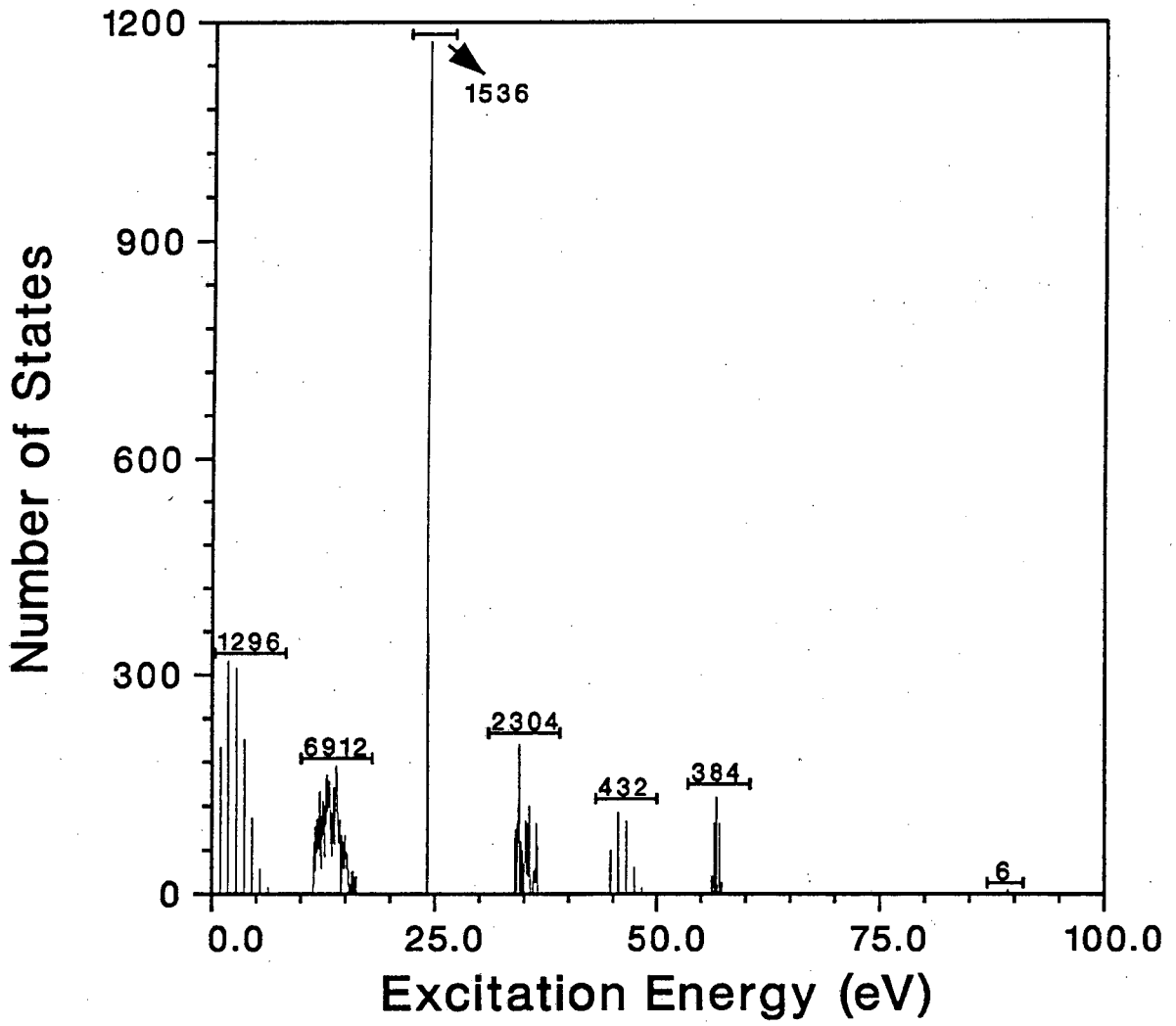
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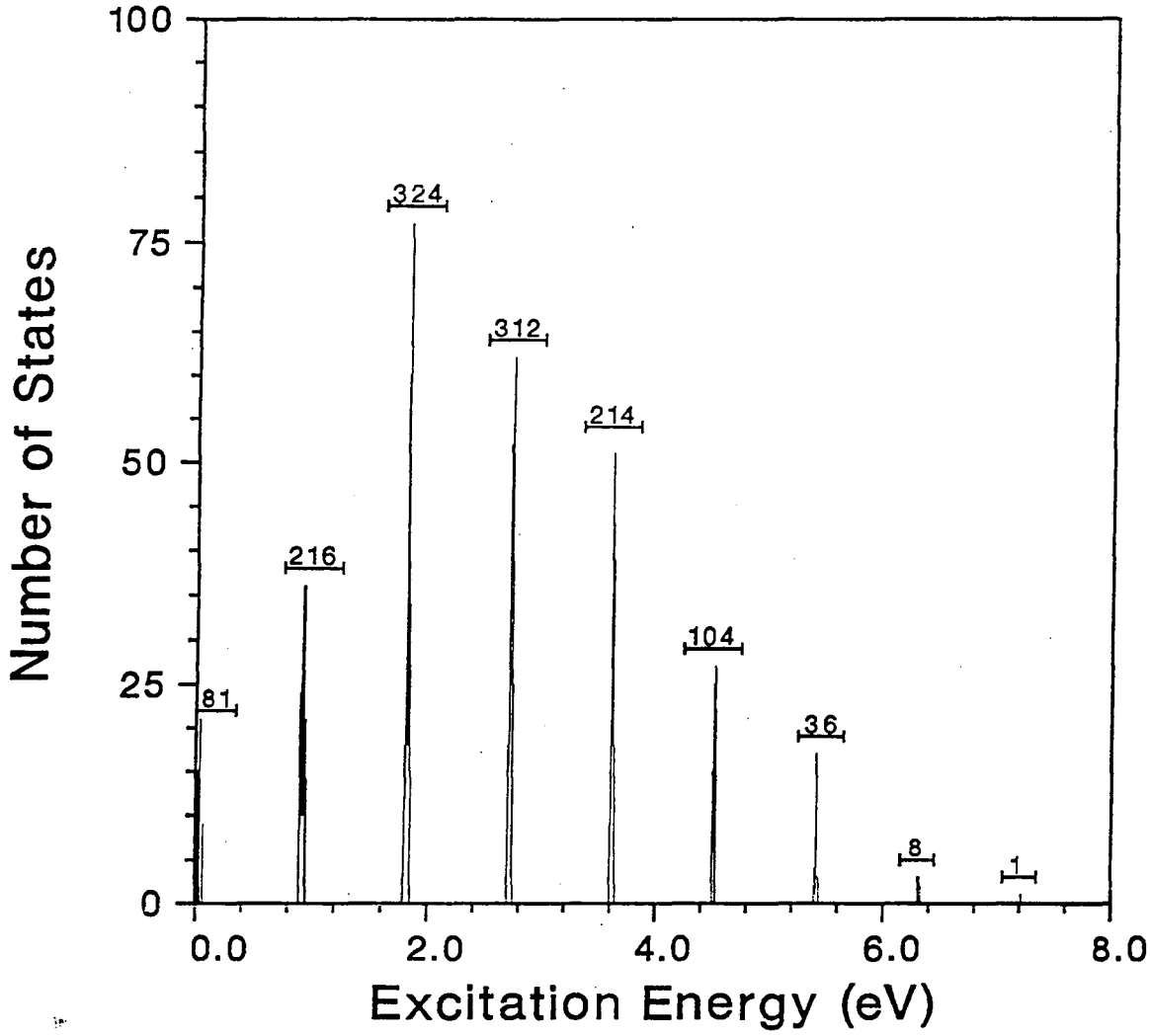
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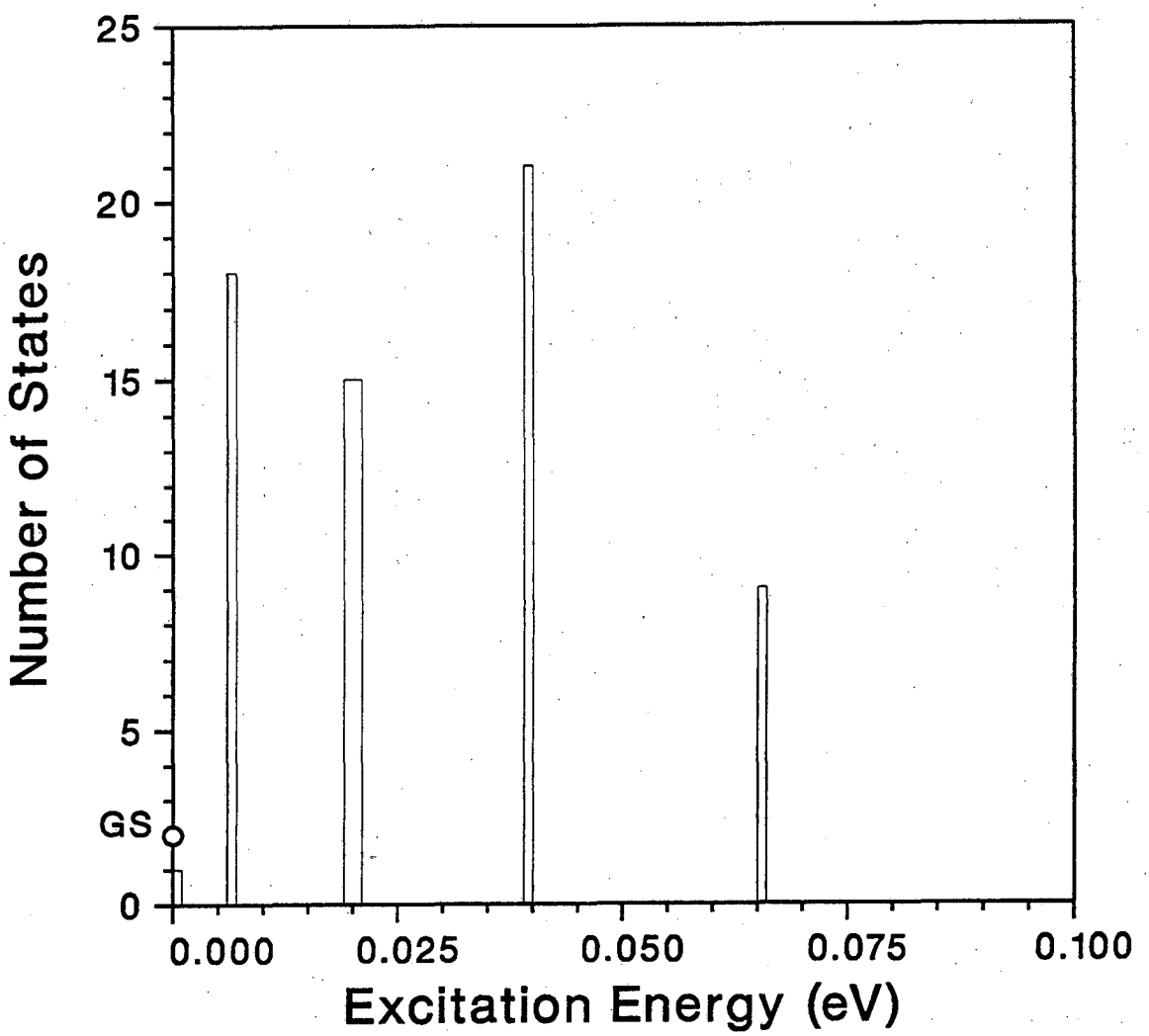
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