

CRITICAL DENSITY IN PERCOLATION PROCESSES

Harvey Scher and Richard Zallen

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lead to relative Franck-Condon factors which bear only a superficial resemblance to the experimental intensities whereas the new parameters give factors which are in good agreement for both ${}^3\Sigma_g^-$ and ${}^1\Delta_g$ molecular states. This has already been noted for the ground state molecular oxygen case,⁹ but the agreement in the case of both transitions is further evidence in favor of the new spectroscopic parameters for $O_2^+({}^2\Pi_g)$ and of our identification of the photoelectron spectrum of $O_2({}^1\Delta_g)$. The sensitivity of the calculated Franck-Condon factors to small changes in spectroscopic parameters may make vacuum ultraviolet photoelectron spectroscopy a useful and simple method for checking these values in the case of other diatomic ions.

By assuming equal cross sections for photoionization of $O_2({}^1\Delta_g)$ and $O_2({}^3\Sigma_g^-)$ we calculate that 10%–12% of the molecular oxygen is in the excited state. However, a more quantitative calibration procedure is planned in order to measure the relative cross sections as these are of some theoretical interest as well as being of importance in upper atmosphere processes.

There should be several additional ionization potentials for $O_2({}^1\Delta_g)$ below the 21.21-eV limit. However, these have not yet been detected although further attempts are being made.

There is an obvious kinetic interest in this technique as a means of following reaction rates. In this respect it would be an extension of the photoionization method already described.¹² There is also reason to believe that radicals may be detected by photoelectron spectroscopy and in other work we have observed spectra of atomic

species as well as vibrational excited nitrogen in its ground electronic state.¹³

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Critical Density in Percolation Processes

HARVEY SCHER AND RICHARD ZALLEN

Xerox Research Laboratories, Rochester, New York 14603

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Percolation processes on infinite lattices are relevant to a variety of physical problems¹ (e.g., dilute ferromagnets²) and have been treated by several authors.^{3–5} In a lattice in which each site is occupied with probability p or vacant with probability $1-p$, and in which adjacent (i.e., nearest neighbor) occupied sites are regarded as connected, there exists a critical probability p_c above which there occur unbounded clusters of connected sites (i.e., the mean cluster size $\rightarrow \infty$ as $p \rightarrow p_c^-$). Estimates for p_c for the basic lattices (all sites equivalent) in two and three dimensions have been obtained by Monte Carlo techniques⁴ and by series expansions⁵: In three dimensions p_c varies from 0.19 for the close-packed fcc and hcp structures to 0.43 for the open diamond structure. In this note we introduce a geometric interpretation of site-occupation probability in terms of a space-occupation probability density ρ corresponding to the packing of spheres (in three dimensions) or circles (in two dimensions). We find that in three dimensions the various critical site probabilities reported for different lattices all correspond to the same critical probability density (fraction of occupied space) of 0.15. In two dimensions the analogous result is found to be 0.44, and in one dimension it is, of course, 1.00.

The clearest way of defining our geometric notion of critical density is within the context of a specific example. In Fig. 1 we display the situation for the

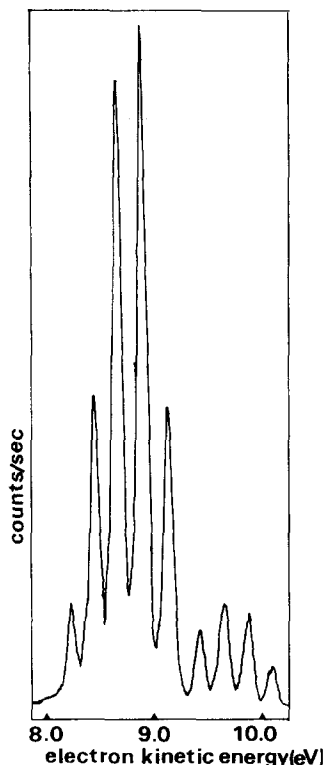


FIG. 1. High-resolution spectrum of lowest ionization potential band of $O_2({}^1\Delta_g)$ and $O_2({}^3\Sigma_g^-)$. Ordinate: counts/sec. Abscissa: electron kinetic energy (in electron volts).

TABLE I. Critical percolation densities in two and three dimensions.

Lattice	Coord. number n	Filling factor f	Critical percolation probability ^a p_c	Critical percolation density ρ_c
Two dimensions				
Triangular	6	0.9069	0.5000	0.4534
Square	4	0.7854	0.59±0.02	0.46±0.02
Kagomé	4	0.6802	0.6527	0.4440
Honeycomb	3	0.6046	0.70±0.02	0.42±0.01
				$\rho_c(2D) = 0.44 \pm 0.02$
Three dimensions				
fcc, hcp	12	0.7405	0.195±0.01	0.144±0.01
bcc	8	0.6802	0.24±0.02	0.163±0.01
sc	6	0.5236	0.31±0.02	0.162±0.01
diamond	4	0.3401	0.43±0.03	0.146±0.01
				$\rho_c(3D) = 0.154 \pm 0.005$

^a See Ref. 5. The errors listed for p_c are twice the standard errors given by these authors. For the triangular and the Kagomé lattices, exact values are available.

two-dimensional honeycomb lattice, an open structure which is threefold coordinated (coordination number n = number of nearest-neighbor sites = 3). We associate with each lattice site a circle of radius equal to half the nearest-neighbor separation. Open circles indicate empty sites, shaded circles indicate filled sites, and linked clusters have been represented by networks of heavy lines. Now p is the fraction of circles which are occupied, and ρ is defined as the fraction of space taken up by the occupied circles. The relationship between ρ and p is dictated by simple geometry: $\rho = fp$, where f is the filling factor for the lattice, i.e., the fraction of space occupied by all of the circles of Fig. 1. The critical density ρ_c is then just fp_c . The filling factor for the open lattice of Fig. 1 is 0.60, compared to 0.91 for the close-packed triangular lattice. In three dimensions f varies from 0.34 for the diamond structure to 0.74 for the two close-packed structures.

Values for ρ_c for the basic lattices in two and three dimensions, based on the best current estimates for p_c , are given in Table I. While p_c varies by over a factor of 2 for the three-dimensional lattices, ρ_c is found to be remarkably constant. A similar result obtains in two dimensions. The obvious implication is that, to a close approximation, ρ_c is independent of lattice structure, depending only on the dimensionality of the space. (In one dimension it is easy to show that $\rho_c = p_c = 1$.) We present this general statement solely as an empirical rule based on the data of Table I; in this note we make no attempt at the underlying explanation.

As an application of this general rule, we treat the case of identical microscopic conducting spheres embedded in an insulating medium. In order to connect this with a lattice problem, consider first the three-dimensional analogs of Fig. 1 with shaded and unshaded

circles representing metallic and insulating spheres, respectively, and with the linkage lines representing conducting paths. The numbers in Table I then specify the critical concentrations (various p_c 's, $\rho_c = 0.15$) of metal spheres needed for the onset, for each ordered array, of conduction on a macroscopic scale. (Note that, as far as conduction is concerned, there is no distinction between the insulating spheres and the interstitial spaces, which together can be viewed as comprising an insulating continuum.) Now consider a disordered mixture of metal and insulating spheres. If we regard the amorphous structure as a superposition of lattice-like local configurations, we are led to the conclusion that $\rho_c = 0.15$ remains applicable. Experiments on binder layer systems, in which conducting particles are randomly dispersed in an insulating medium, are consistent with this expectation; the onset of macroscopic conductivity occurs at about the critical density of 15% by volume of conducting material.⁶

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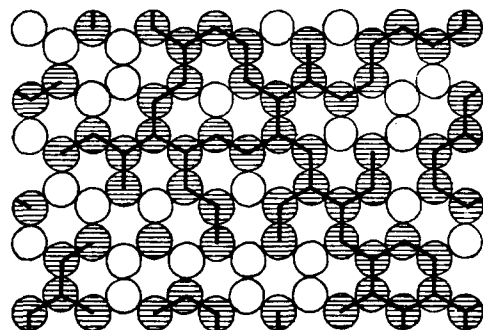


FIG. 1. Percolation on a two-dimensional honeycomb lattice. Shaded circles indicate filled sites, open circles indicate empty sites, and linked clusters are shown connected by heavy lines.

in this problem, and Professor E. W. Montroll for helpful discussions and for accurately guiding us to the relevant literature.

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Infrared and Single-Crystal Raman Spectra and Vibrational Assignments for $\text{Cs}_2\text{LiCo}(\text{CN})_6$ *

BASIL I. SWANSON† AND L. H. JONES

*University of California, Los Alamos Scientific Laboratory,
Los Alamos, New Mexico 87544*

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In conjunction with studies of bonding in metal cyanide complexes being carried out in this laboratory, we are interested in the potential constants for the cobaltihexacyanide ion. While infrared¹⁻³ and Raman⁴ spectra are available for $\text{K}_3\text{Co}(\text{CN})_6$ there are a number of questionable assignments for this salt. The E_g Co-C stretching mode has not been definitely assigned in either the solid state or in aqueous solution.⁴ In addition, the assignments of both F_{1u} and F_{2g} C-Co-C deformation modes for the solid are uncertain because of the large number of lattice modes in the low-energy region.

In an x-ray diffraction study of $\text{Cs}_2\text{LiCo}(\text{CN})_6$, Wolberg⁵ has shown the space group to be $Fm\bar{3}m$ and the

$\text{Co}(\text{CN})_6^{-3}$ site symmetry to be O_h . We have carried out a factor group analysis following the procedure of Bhagavantam and Venkatarayudu,⁶ which shows that there is one inactive rotatory mode (L_1, F_{1g}) and three translatory modes (L_2 and L_3, F_{1u} , infrared active only and L_4, F_{2g} Raman active only). In the Raman the F_{2g} symmetry modes may be distinguished from E_g and A_{1g} modes using single crystal polarization data. With 180° excitation, the polarization orientation of the F_{2g} modes is $Z(YX)Z$ and that of the E_g and A_{1g} modes is $Z(XX)Z$.⁷ Thus the assignments are greatly simplified.

Pale yellow single crystals of $\text{Cs}_2\text{LiCo}(\text{CN})_6$ were obtained by slow evaporation of a solution prepared by mixing the individual alkali salts.⁸ The Raman spectrum was obtained on a Cary 81 using He-Ne laser excitation (6328 Å, Spectra Physics 125). The infrared spectrum from 4000 to 35 cm^{-1} was obtained on a Perkin-Elmer 521 and Beckman IR-11 calibrated with standard gases.^{9,10} The observed Raman and infrared fundamentals, polarization, and possible assignments are given in Table I.

The assignment of the active internal modes above 400 cm^{-1} is straightforward and presents little difficulty. The A_{1g} and E_g C≡N stretching modes cannot be distinguished on the basis of polarization data. However, the relative intensities and similarity to solution data for $\text{K}_3\text{Co}(\text{CN})_6$ suggest that the totally symmetric C≡N stretch, ν_1 , be assigned to the higher-frequency band.

The Raman spectrum exhibits two $Z(XX)Z$ polarized peaks in the Co-C stretch region which can be assigned to ν_2 and ν_4 . As was the case with the C≡N stretching vibrations, ν_2 and ν_4 cannot be distinguished. However, the high relative intensity of the 431 cm^{-1} feature suggests that this band can be assigned to the totally symmetric stretch, ν_2 . Interestingly, the Co-C E_g stretching mode is observed for $\text{Cs}_2\text{LiCo}(\text{CN})_6$ while both solution and solid state spectra of $\text{K}_3\text{Co}(\text{CN})_6$ give no conclusive evidence for this mode. Possibly the

TABLE I Observed Raman and infrared fundamentals (cm^{-1})^a

Infrared		Raman			Assignment	
...	...	46.8	m	$Z(XY)Z$	F_{2g}	L_4
57.8	vs(br)	F_{1u}	L_3
162.3	ms	F_{1u}	$\nu_9(\text{CCoC } \delta)$
...	...	189.9	vs	$Z(XY)Z$	F_{2g}	$\nu_{11}(\text{CCoC } \delta)$
198.6	w	F_{1u}	$\nu_9 + L_3$
305	vs	F_{1u}	L_2
...	...	418.1	mw	$Z(XX)Z$	E_g	$\nu_4(\text{CoC str})$
429	vs	F_{1u}	$\nu_8(\text{CoC str})$
...	...	431.1	s	$Z(XX)Z$	A_g	$\nu_2(\text{CoC str})$
...	...	484.6	vw	$Z(XY)Z$	F_{2g}	$\nu_{10}(\text{CoCN } \delta)$
566.0	m	F_{1u}	$\nu_7(\text{CoCN } \delta)$
2141.8	vvs	F_{1u}	$\nu_6(\text{CN str})$
...	...	2150.8	ms	$Z(XX)Z$	E_g	$\nu_8(\text{CN str})$
...	...	2161.6	s	$Z(XX)Z$	A_g	$\nu_1(\text{CN str})$

^a Several weak features were observed and these will be reported later.