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Final Report on NASA grant no. NAG 2-171

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Abstract

The work associated with NASA grant no. NAG 2-171 has been directed toward understanding the high pressure properties of molecular solids and molecular surfaces deposited on heterogeneous substrates. The motivation for this work, apart from expanding our basic knowledge about these systems, has been to understand and predict the properties of new materials synthesized at high pressure, including pressure induced metallic and superconducting states. As a consequence, it has been our intention to also provide information about the states of matter of the Jovian planets and their satellites, which are natural high pressure laboratories.

The work on molecular surfaces and finite two and three dimensional clusters of atoms and molecules is connected with the composition and behavior of planetary atmospheres and on the processes involved in forming surface layers, which is vital to the development of composite materials and microcircuitry.

Progress Report:

During the period of this grant eight articles were published in international refereed journals. Copies of these articles are included in this final report and in this section a brief summary of the major accomplishments achieved in those works will be presented.

A. "Prediction of structures and magnetic orientations in Solid α and $\beta-O_2$," Phys. Rev. B <u>28</u>, 2166 (1983); "Ground State Structural and Magnetic Properties of Solid α and $\beta-O_2$," Int. J. Quantum Chem. <u>17</u>, 491 (1983).

In this work we established that the Heisenberg magnetic inter-action is responsible for stabilizing the α phase over $\beta-O_2$ at low temperatures and pressures, as had earlier been speculated but hereto-fore unproven. The predicted zero pressure sublimation energy,[1] lattice parameters,[2] and molar volume[2] were found to be in good agree-ment with experiment as was the second virial coefficients.[3] On the basis of energetic and structural results it was concluded that the quasihelical structure with long range order is the most likely magnetic arrangement for $\beta-O_2$. Recent neutron scattering experiments[4] support this conclusion. Also calculated were the zero pressure bond lengths, libron frequencies and the dispersion curves.

B. "Pressure dependence of intramolecular mode frequencies in solid N_2, O_2, and CO_2," Phys. Rev. B <u>27</u>, 6439 (1983); "Pressure dependence of intramolecular vibrational mode frequencies in simple molecular crystals," Proceedings of the eighth symposium on Thermophysical Properties, edited by J. V. Sengers, Vol. II, the American Society of Mechanical Engineers, N.B.S., Gaithersburg, MD, June 15-18 (1981).

In this work a simple classical perturbation theory was formulated to calculate the frequency change with pressure of the internal vibra-tional modes (vibrons) in solids composed of linear molecules. It was

argued that the pressure dependent crystal field of the solid, embodied in the total intermolecular potential energy per molecule, slightly perturbs the intramolecular potential of the molecule from its gas phase value, changing the intramolecular force constants and thus the vibron frequency. It was found that the pressure dependence of the vibron frequencies is sensitive to the short ranged, repulsive part of the intermolecular potential and thus provides a sensitive test of the insitu intermolecular pair potential. It was also found that intermolecular potentials that best reproduce existing pressure-volume relations also give the best predictions for the pressure dependence of the vibron frequencies, which were found to be in good agreement with experimental data, mostly determined from diamond cell Raman and Infrared absorption measurements.[5] Results were shown for CO_2, O_2, and N_2.

C. "Calculation of high pressure phase transitions in solid N_2 and the pressure dependence of intramolecular mode frequencies," Phys. Rev. B 28, 1095 (1983); "Prediction of a new phase in solid N_2 at high pressure," Phys. Rev. B 26, 5996 (1982).

In our first paper on the high pressure properties of solid N_2 at low temperature we proposed the existence of a phase transition from the γ phase into an $R\bar{3}m$ structure, similar to β-O_2, at $P \simeq 40$ kbar. This was determined by comparing the free energy of these two structures. Subsequent Raman scattering measurements[6] showed that there is in fact a lower energy structure for which a phase transition occurs at $P \simeq$ 20 kbar. The existence of two vibron branches in this new phase showed that the structure is neither $R\bar{3}m$ or γ-N_2. In fact, the two branches gave an indication that the structure was similar to the cubic $Pm3n$ phase with 8 molecules per unit cell, known to exist at high pressures

near room temperature.[6] However, the observed phonon peaks indicated that the structure was not cubic. Consequently, we considered a rhombohedral distortion of the Pm3n structure and minimized the lattice energy with respect to the distorted lattice parameters and the positions and orientations of the molecules in the unit cell. The results showed that this rhombohedral structure is preferred over the γ-N_2 structure above 19.2 kbar, in good agreement with experiment.[2] The calculated structure is in fact $\overline{R3}c$, which has recently been confirmed by recent x-ray diffraction measurements.[7] We also calculated the pressure dependence of the two vibron branches, which were in qualitative agreement with experiment, but the calculated frequencies were considerably higher than experiment at high pressures. Since the calculated pressure-volume relation was also higher than experiment,[8] this lack of quantitative agreement was attributed to the repulsive part of the intermolecular pair potential used, which we believe is too stiff. Nevertheless, the overall agreement with experiment is quite satisfactory and establishes the character of this low temperature, high pressure phase of N_2.

D. "Lattice dynamics of solid I_2 under pressure," J. Chem. Phys. **79**, 3018 (1983).

The structure, phonon, libron, and vibron frequencies of solid I_2 at low temperature under pressures $0 \leq P \leq 210$ kbar has been experimentally determined.[9] These results are exciting in that it is the first clear evidence of a pressure induced transition from a molecular insulator to an atomic conductor, which takes place at 210 kbar. Such transitions are predicted in all diatomic insulators at sufficiently high pressure. Calculations are difficult because it is well known

that pressure induced charge rearrangement in the molecule is signifi-
cant, so that the determination of the effective intermolecular pair
potential in the solid is very complicated, especially since it is
quite different from that determined from gas phase properties. In
this work we developed a multi-parameter potential, including charge
transfer terms, and fitted these parameters so that a best fit to
experimental structural and dynamic data could be obtained at all pres-
sures. The results are in good agreement with experiment but they are
not completely satisfying because of the empirical nature of the poten-
tial.

E.   "Predictions for partial and monolayer coverages of O_2 on graphite,"
     J. Chem. Phys. __77__, 1035 (1982).

In this work the equilibrium structures and the energy per molecule
were calculated as a function of surface density, using a pattern recog-
nition optimization scheme. It was found that the lowest energy con-
figuration forms a centered rectangular structure with all molecular
axes collinear and lying in the plane of the substrate. This result
was contrary to previous neutron scattering interpretations[10] but
subsequent measurements[11] proved it to be correct. At higher surface
densities another minimum in the energy occurs in which the lattice is
triangular and the molecular axes are all collinear and point normal
to the substrate plane. These results are consistent with the observed
ϵ and η phases found at higher surface densities. Thus, theory and
experiment are in good qualitative and quantitative agreement.

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