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J. F. Ogilvie

Citation: The Journal of Chemical Physics **59**, 3871 (1973); doi: 10.1063/1.1680569
View online: http://dx.doi.org/10.1063/1.1680569
View Table of Contents: http://aip.scitation.org/toc/jcp/59/7
Published by the American Institute of Physics

Comments

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 59, NUMBER 7 1 OCTOBER 1973

Infrared absorption of hydrogen atoms in solid argon and krypton

J. F. Ogilvie
Department of Chemistry, Memorial University of Newfoundland, St. Johns's, Newfoundland, Canada
(Received 19 May 1972)

Bondybey and Pimentel[1] have reported experimental absorption spectra which they attribute to hydrogen atoms trapped in solid argon and krypton at 15 °K. The evidence for the nature of the carrier is convincing; in fact spectra obtained during past deuterium-atom discharge experiments in solid argon at temperatures from 8 to 21 °K in this laboratory corroborate this assignment. Our failure to detect the corresponding hydrogen-atom absorption is consistent with the reported small half-time[1] and with our spectroscopic scanning conditions.

The purpose of this Comment is to question the deduced nature of the trapping site within the solid matrices. Bondybey and Pimentel have concluded that their evidence is consistent with trapping in interstitial sites of octahedral symmetry. However their principal justification for such an assignment seems to be a computation for hydrogen atoms in solid neon for which no spectra are observed. In previous experiments on trapped hydrogen atoms in argon matrices, detected by electron magnetic resonance methods, Foner, Cochran, Bowers, and Jen[2] have deduced the existence of three trapping sites. One of these sites, the only one occupied as a result of deposition from discharge flow production of hydrogen atoms, was associated with a substitutional position in the latlatice; stabilization of hydrogen atoms in such sites was successful until temperatures near 39 °K. The other two sites, one of which was variably produced, were additionally present when hydrogen iodide photolyzed *in situ* was the source of H atoms; instability at these sites occurred at 12 and 23 °K. Adrian's theoretical treatment[3] gave satisfactory agreement with the consistently present additional site being octahedral interstitial in nature. By comparison of flow discharge production methods, one can associate the same site with both ESR[2] and ir[1] experiments, therefore presumably the *substitutional* site. The temperature evidence from the ESR experiments[2] and from our experiments fully corroborate this conclusion. If the occupancy of more than one site occurred in the ir experiments, additional spectral lines ought to have been detected, as the large wavenumber shift from argon to krypton matrices indicates considerable sensitivity of the vibrational wavenumber to the properties of the site. On the other hand, the variable presence of the third site, in photochemical ESR experiments,[2] and the occupancy of only (presumably) octahedral interstitial sites in other photolytic experiments,[4] together with the known metastable hexagonal phase of solid argon which can be stabilized by impurities,[5] suggest that the straightforward analysis given here may be an oversimplification. Comparable warmup experiments with infrared detection would facilitate comparison of the sites occupied in experiments of Bondybey and Pimentel with previous results of this kind.[2]

A possibly more interesting problem is the discrepancy between observed absorption wavenumbers of H and D in argon and those predicted on the basis of the electronic absorption spectrum of the impurity atoms.[6,7] The observed wavenumbers, 905 cm^{-1} for H and 644 cm^{-1} for D, are more than a factor of 3 larger than the deduced values, 273 or 266 cm^{-1} for H and 193 or 186 cm^{-1} for D.[6,7] The theoretical analyses which provided the predictions have no obvious flaws which could account for the extent of the discrepancy, except that the theoretical models adopted must now be suspect. One hopes that further theoretical work in the light of all available experimental and theoretical results, will resolve these problems. Certainly the simplicity of the hydrogen atom as a quantum species and the applicability of perturbation theory would seem to make this system very attractive for appropriate calculations.

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