1975 (unpublished).

[10] M. Héritier and P. Lederer, to be published.

[11] G. Montambaux, P. Lederer, and M. Héritier, to be published.

[12] M. V. Feĭgel'man, Pis'ma Zh. Eksp. Teor. Fiz. 27, 491 (1978) [JETP Lett. 27, 462 (1978)].

[13] J. M. Delrieu, private communication.

[14] S. Alexander and P. A. Pincus, to be published.

[15] J. Friedel, private communication; F. Cyrot, Adv. Phys. 16, 393 (1967).

[16] M. Nielsen, J. P. McTague, and W. Ellenson, J. Phys. C 4, 10 (1977).

[17] A. I. Ahonen, T. A. Alvesalo, T. Haavasoja, and M. C. Veuro, J. Phys. C 6, 285 (1978).

[18] M. T. Béal-Monod, private communication.

[19] Spanjaard, Mills, and Béal-Monod, Ref. 5.

[20] J. B. Sokoloff and A. Widom, in Proceedings of the International Conference on Quantum Crystals, Fort Collins, Colorado, 1977 (unpublished); K. Maki, private communication.

Nuclear Spin Relaxation of Hydrogen in a Solid Argon Matrix

James E. Kohl, Myron G. Semack, and David White
Department of Chemistry and Laboratory for Research of the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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T_1 and T_2 data at 5.5 K measured at 33 MHz are reported for solid matrices of normal hydrogen in argon with hydrogen mole fraction $0.004 < x < 0.33$. The results are interpreted in terms of a theory developed by Ebner and Myles in their study of solid ortho-para hydrogen mixtures. The crystal field consistent with the data is estimated to be 0.2 K. The T_2's, taken from the far-infrared detectors, are smaller than those predicted.

The first application of proton magnetic resonance to matrix-isolated molecules was recently carried out in this laboratory.[1] The experimental apparatus described in detail in Ref. 1 has now been used to prepare solid mixtures of normal hydrogen and argon with hydrogen mole fractions $0.004<x<0.33$. For these experiments a slow deposition rate ($\sim 0.3\times10^{-3}$ mole/min) was chosen to prevent excessive warming of the cesium iodide sample tube. It was found that the sample tube must be maintained at temperatures less than 7 K in order to produce solid samples with mole fractions of hydrogen essentially that of the original gaseous mixtures as verified by the observed signal amplitudes.

Because of the relatively fast spin-lattice relaxation time T_1 in this system, we were able to observe the signal-averaged free-induction decays during the filling or matrix-deposition process. Typical results are presented in Fig. 1 where the signal amplitude multiplied by the temperature, to correct for changes in temperature during deposition, is plotted against the total amount of sample sprayed into the tube up to that time. The sharp edge at the top of the curve is coincident with the visual observation of a full sample tube, whereas the linearity of the curve up to that point shows that the filling is uniform and that the interior of the sample is in thermal equilibrium with the cell even when heat is being removed by the surroundings during deposition.

The systematic variation of the observed T_1 (at 33 mHz) with changes in orthohydrogen concentration c (see Fig. 2) and the observation of the expected absolute signal amplitude indicates that solid mixtures of hydrogen in argon with x as great as 0.33 can be prepared using this method even though the solubility of hydrogen in condensed rare gases at low temperatures is known[2] to be orders of magnitude smaller. If, for exam-

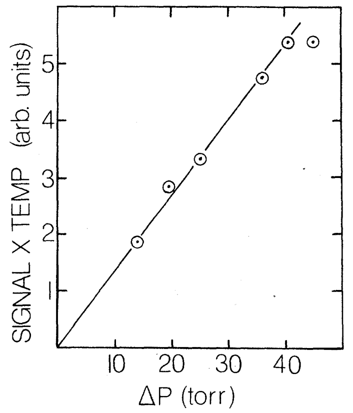

FIG. 1. The Curie-law–corrected signal amplitude observed during deposition of a 2% n-H_2 sample plotted vs total change in pressure from a 1.5-liter gaseous sample volume.

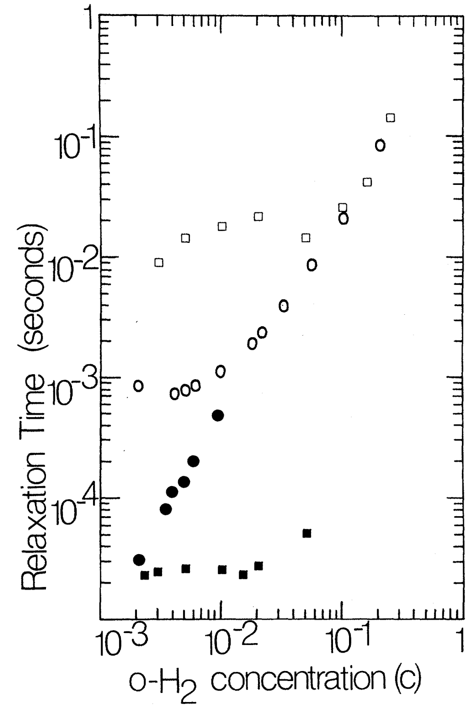

FIG. 2. Nuclear spin relaxation vs o-H_2 mole fraction: open squares, T_1 of o-H_2 in argon at 5 K and 33 mHz; open circles, T_1 of o-H_2 in p-H_2 at 4.2 K and 30 mHz (taken from Ref. 3); closed squares, T_2^{intra} of o-H_2 in argon at 5 K and 33 mHz, closed circles T_2^{intra} of o-H_2 in p-H_2 at 4.2 K and 30 mHz (taken from Ref. 3).

ple, the components of the solid mixtures were to have undergone phase separation, the T_1 observed would have been characteristic of normal H_2 which is orders of magnitude larger.[3,4]

It should be noted that in these experiments as in the earlier orthohydrogen (o-H_2 in parahydrogen (p-H_2) experiments of Hardy and Gaines[3] the thermal relaxation is not characterized by a single relaxation time. The plot of the quantity $\ln\{[S(\infty)-S(\tau)]/S(\infty)\}$ versus τ, where $S(\tau)$ is the signal amplitude following a 180°-τ-90° pulse sequence, exhibits considerable curvature which is largest at the highest and lowest concentrations where the linewidths are largest. In Fig. 2 the initial slopes of the relaxation curves are plotted as a function of orthohydrogen concentration.

Recent experimental[4] and theoretical[5-7] interest in the variation of the NMR T_1 and T_2 of o-H_2 in p-H_2 with o-H_2 concentration, we well as earlier work cited in the references given above, has inspired the present investigation. By replacing much of the p-H_2 with ^{40}Ar, zero nuclear spin, the crystal field experienced by the o-H_2 is altered without significantly changing the ortho-ortho separations since the nearest-neighbor distances in solid H_2 and argon are very similar. Thus, theoretical models of the o-H_2 in p-H_2 system can be tested under conditions where one of the important parameters in the theory has been modified by substitution in the lattice of the spherically symmetric but polarizable p-H_2 species with a different spherically symmetric polarizable species, namely argon.

In the temperature and concentration region reported here, the o-H_2 nuclear spin-lattice relaxation is dominated[6] by *intra*molecular magnetic interactions which are modulated by molecular rotational motion. Myles and Ebner[7] have very recently modified their earlier theory[6] to include the effects of the crystalline and external magnetic fields on the rotational autocorrelation functions and thus on the nuclear spin relaxation. In the absence of these fields the autocorrelation functions,[6] $G_{l,m}(\tau)$, are determined by the electric quadrupole-quadrupole (EQQ) interactions between o-H_2 molecules. Here $\tau=\hbar^{-1}(140\pi/27)^{1/2}\Gamma t$ is the dimensionless time introduced in Ref. 6 and Γ is the strength of the EQQ interaction which is modified by the presence of p-H_2 or argon and taken to be 0.91 K in Ref. 7 and in the present work.

Myles and Ebner[7] show that the autocorrelation functions are modified by the crystalline and magnetic fields according to their Eq. (10) so that

$$G_{lm}'(\tau)=e^{imb\tau}\cos(V_c\tau\delta_{m,\pm1})G_{lm}(\tau), \qquad (1)$$

where b is proportional to the external field and V_c is the crystal-field splitting of the $m_J=\pm1$ levels from the $m_J=0$ level. In Eq. (1) we have replaced t by τ so that both b and V_c are specified in the reduced units discussed in Ref. 7.

From Eq. (1) we see that the magnetic field shifts the spectral density functions whereas the crystal field splits the $m=\pm1$ spectral density functions and leaves the others unchanged. As stated by Myles and Ebner[7] the crystal field can affect the nuclear spin relaxation times significantly only if its magnitude is large enough to resolve the peaks in the spectral density functions. Otherwise the relaxation times follow the $c^{5/3}$ law which is valid at the highest concentrations in these studies as in the solid-H_2 studies[3,4] where the spectral density functions are quite broad. While at these temperatures and orthohydrogen concentrations the crystal structure for solid H_2 is hcp, in the H_2-Ar system assuming hydrogen molecules occupy substitutional sites in the argon matrix, which is reasonable since nearest-neighbor distances in the pure component solids are nearly identical, the crystal structure is fcc. The theory[7] need not, however, be modified to treat the fcc structure since in both crystal lattices the crystal field, which is octahedral in the fcc lattice,[8] leaves the $m_J = \pm 1$ states of o-H_2 degenerate while splitting them from the $m_J = 0$ level. For the octahedral field this can readily be seen by examining the appropriate diagonal matrix elements in Devonshire's original paper.[8]

In this Letter the detailed calculation of the concentration dependence of T_1 and T_2 is not undertaken. Instead the magnitude of the crystal-field splitting is estimated by noting the concentration at which T_1 begins to deviate from the $c^{5/3}$ line representing the higher concentrations of Fig. 2. The justification for this procedure is the exact calculation for o-H_2 in p-H_2,[7] where it is shown this concentration represents the point at which the peaks in the spectral density function $g_{11}(\omega)$ due to V_c become resolved. Since, at higher concentrations, T_1 for o-H_2 in argon lies within experimental error on the same line as T_1 for o-H_2 in p-H_2, the EQQ coupling constant Γ is roughly the same in the two systems.

Figure 3 shows the spectral density function $g_{11}(\omega)$ for $c = 0.1$ and $V_c = 0.2$ K calculated by using Eq. (1) to modify the autocorrelation function given in Fig. 1 of Ref. 6 and taking the Fourier transform. Note that this value of V_c just resolves the two peaks. Thus the Ebner-Myles theory as applied to the data of Fig. 2 would yield a value of the crystal field in the H_2-Ar system of about 0.2 K.

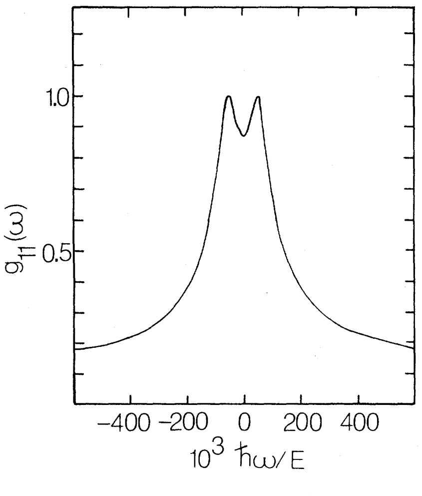

FIG. 3. The spectral density function of $g_{11}(\omega)$ in arbitrary units at $c = 0.1$ for $\Gamma = 0.91$ K and $V_c = 0.2$ K vs the dimensionless frequency ω' (see Ref. 7). One unit along the abscissa equals one unit in Fig. 1 of Ref. 7.

As the concentration is lowered below $c = 0.02$, T_1 begins to decrease again which is expected since only the autocorrelation functions with $m = \pm 1$ are affected by the crystal field. Such a maximum was not observed in the o-H_2 in p-H_2 system, where the crystal field is much smaller ($V_c = 0.02$ K).[4,7,9] The very recent work of Conradi, Luszczyinski, and Norberg[10] extends the present experiment to much lower concentrations where T_1 is expected to again increase with decreasing concentration from magnetic field effects. A comparison of the data in Fig. 2 with a detailed calculation of the concentration dependence of T_1 would provide an interesting check of the Ebner-Myles theory.

In addition to the T_1 data, T_2^{intra} is plotted in Fig. 2. These values of T_2^{intra} are calculated by correcting the T_2^{obs} measured from the far-infrared detectors for intermolecular spin-spin broadening so that they can be compared to the intramolecular T_2's calculated in Ref. 7 (see Table I). At concentrations higher than those given in Table I the intermolecular effects become very large so that T_2^{intra} cannot be satisfactorily extracted from the data.

As noted in Ref. 7 the T_2 data of Buzarak, Chan, and Meyer[4] bends below the $c^{5/3}$ line whereas the theory[7] predicts bending above this line for all values of the adjustable parameters. In the H_2-Ar system, the effect is more dramatic and at low concentrations T_2^{intra} falls well below the $c^{5/3}$ line is essentially independent of c. The low experimental value of T_2^{intra} may be attributed to a static broadening of the NMR line due to a breakdown of the high-temperature approximation and

TABLE I. Experimental T_2^{intra} of o-H_2 in solid argon at 5 K as a function of concentration.

c	$1/T_2^{\text{obs}}$ (msec^{-1})	$1/T_2^{\text{inter}}$[a] (msec^{-1})	$1/T_2^{\text{intra}}$[b] (msec^{-1})	T_2^{intra} (μsec)
0.050	34.8	14.3	20.5	48.8
0.020	40.8	5.72	35.1	28.5
0.015	46.7	4.29	42.4	23.6
0.010	42.7	2.86	39.8	25.1
0.005	39.2	1.43	37.8	26.5
0.003	40.0	0.858	39.1	25.6
0.0023	42.9	0.658	42.2	23.7

[a] Calculated using the same method as Ref. 4.
[b] $1/T_2^{\text{intra}} = 1/T_2^{\text{obs}} - 1/T_2^{\text{inter}}$.

an enhanced population of the ground state of the crystal field. However, to account for the very short T_2^{intra} observed a crystal field of nearly 2 K would be required, which is rather large compared to the value estimated from the T_1 data. The low-concentration T_2 data thus still remains to be explained.

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[1] J. E. Kohl, M. G. Semack, and David White, J. Chem. Phys. 69, 5378 (1978). This work, together with the ^{13}C work of K. W. Zilm, R. T. Conlin, D. M. Grant, and J. Michl, J. Am. Chem. Soc. 100, 8038 (1978), represents the first application of NMR to matrix-isolated molecules.

[2] C. S. Barrett, L. Meyer, and J. Wasserman, J. Chem. Phys. 45, 834 (1966).

[3] W. Hardy and J. R. Gaines as quoted in C. C. Sung, Phys. Rev. 167, 271 (1968).

[4] R. F. Buzerak, M. Chan, and H. Meyer, J. Low Temp. Phys. 28, 415 (1977).

[5] C. W. Myles and C. Ebner, Phys. Rev. B 11, 2339 (1975), and 12, 1608(E) (1975).

[6] C. Ebner and C. W. Myles, Phys. Rev. B 12, 1638 (1975).

[7] C. W. Myles and C. Ebner, Phys. Rev. B (to be published).

[8] A. F. Devonshire, Proc. Roy. Soc. London, Ser. A. 153, 601 (1936).

[9] J. Constable and J. R. Gaines, Solid State Commun. 9, 155 (1971).

[10] Mark S. Conradi, K. Luszczyinski, and R. E. Norberg, private communication.

Evidence of the Autoionizing Character of Biexcitons

D. S. Chemla, A. Maruani, and E. Batifol
Centre National d'Etudes des Télécommunications, Laboratoire Associé au Centre National de la Recherche Scientifique, 92220 Bagneux, France

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The highly structured profile of the Γ_1 biexciton level of CuCl is studied experimentally by resonant coherent nonlinear scattering. A theoretical model is presented which accurately describes the Γ_1 biexciton line shape in terms of a Fano interference, evidencing the autoionizing character of biexcitons.

In a previous Letter[1] we have reported the direct observation of the excitonic molecule level in cuprous chloride by a resonant coherent and degenerate nonlinear light scattering. In this process the interaction between "pump" and "test" beams in a thin slab of CuCl gives rise to the third-order polarization,

$$\vec{P}_s(\omega)=\epsilon_0\chi^3(-\omega;\omega,\omega,-\omega)\vdots\vec{E}_p(\omega)\vec{E}_p(\omega)\vec{E}_t^*(\omega), \tag{1}$$

which in turn radiates a collimated "signal" beam in the direction $\vec{k}_s=2\vec{k}_p-\vec{k}_t$ [the notations of Ref. 1 have been used]. This type of spectroscopy has revealed two features of the biexciton level unsuspected so far: (i) the very asymmetric line shape of the resonance and (ii) the highly nonlinear power dependence of the scattering.

The present Letter concentrates on the unusual line shape of the first-order scattering. New experimental data and a theory are presented. This latter explains the observed asymmetric line shape of the biexciton level in terms of a Fano interference.[2]

A detailed description of the experiment is given elsewhere.[3] Compared to the data presented in Ref. 1, a highly improved signal/noise ratio has been obtained by use of a double synchronous detection method. Typical recordings of the ratio $\rho=I_s(l)/I_t(0)$ of the outgoing signal beam intensity to that of the incoming test beam as a function of the dye-laser frequency are shown in Fig. 1(a) and 2(a), respectively, for two high-purity CuCl samples with thicknesses $l=80$ μm and $l=200$ μm. Both exhibit a sharp dip at $\hbar\omega=3.1860$ eV, i.e., half the energy of the biexciton W_{X2} as observed in two-photon absorption[4] (TPA); this dip is surrounded by two humps, about 1.5×10^{-3} eV apart,