

## Nuclear Spin Relaxation and Double Resonance in HD Gas

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Nuclear magnetic double-resonance experiments were performed on a gaseous sample containing a mixture of HD and CO<sub>2</sub> at high pressure by observing the spin-spin multiplet in the proton-resonance spectrum and irradiating either the deuteron transitions or some of the proton transitions. The spectra show features arising from spin relaxation in HD. These features are analyzed by using the density-matrix theory of double resonance, assuming "strong"- and "weak"-collision models for the system. The equation of motion of the spin density matrix is exactly of the same form for both collision models, the only distinction coming from the dependence of the correlation times on the transformation properties of the lattice operators and on the quantum numbers characterizing the lattice states. The results of the analysis of HD double-resonance spectra indicate that the collisions in this case are "strong." The cross products between lattice terms which transform identically but belong to two different relaxation mechanisms make significant contributions to some of the correlation functions involved and thereby affect the final results.

### INTRODUCTION

NUCLEAR magnetic double-resonance spectra usually exhibit features that arise from modification of the transition probabilities between stationary states and of the lifetimes of these states by the irradiating field. The analysis of relaxation effects in double-resonance spectra provides information about the relaxation mechanisms in a spin system and their relative contributions.<sup>1</sup> Such information can usefully supplement the knowledge gained from direct relaxation-time measurements. The efficiency of a spin-lattice interaction in producing spin relaxation is determined by the magnitude of the interaction and the spectral densities of the correlation functions of the lattice operators due to molecular motions.<sup>2,3</sup> In systems containing a large number of spins the interactions that contribute to spin relaxation are numerous, and include both intramolecular and intermolecular interactions. The analysis of relaxation effects in double-resonance spectra in such cases is concerned primarily with the determination of the origin and relative importance of the different spin-lattice interactions<sup>1,4,5</sup> and it is difficult to obtain explicit information on the molecular reorientation processes. In dilute gaseous samples of small molecules where the interactions mediating spin relaxation are intramolecular in origin<sup>2,3</sup> and the various interaction parameters for free molecules are accurately known from other sources,<sup>6</sup> the study of relaxation and co-

herence effects in double-resonance spectra may reveal some features of collisional processes responsible for molecular reorientation.

The investigation of intermolecular forces and molecular motion in gases by the study of spin relaxation is well known. Considerable experimental and theoretical work has been done on the proton relaxation time in orthohydrogen as a function of temperature, pressure, and impurity concentrations.<sup>2,7-14</sup> These studies have shown that the collisions in H<sub>2</sub> are "weak" in the sense that the rotational transition probabilities per collision are small. More recently Hardy<sup>15</sup> has extended these measurements to HD and D<sub>2</sub> and also increased the range of temperature and pressure used. The results on HD, which are of particular importance in relation to the present work, indicate that the collisions in this case are significantly stronger than those in H<sub>2</sub>. In all these studies the experiments are confined either to the direct measurement of relaxation times or to the determination of linewidths of magnetic-resonance signals. In the case of HD there is an additional structure in both proton- and deuteron-resonances arising from indirect spin-spin coupling.<sup>16,17</sup> This fine structure was not resolved in the experiments of Hardy.<sup>15</sup> The analysis of relaxation effects in double-resonance spectra under high resolution is therefore a method, independent of the above, of deriving information about spin relaxation in favorable cases.

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<sup>14</sup> C. S. Johnson, Jr., and J. S. Waugh, *J. Chem. Phys.* **36**, 2266 (1962).

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In this paper the results of double-resonance experiments on HD in the gas phase are presented. These experiments were done by irradiating the various components of the completely resolved multiplet structure due to spin-spin coupling. The relative intensities of double-resonance transitions depend on the details of the spin relaxation. These features were analyzed by using the density-matrix method that has been described in detail.<sup>18</sup> The method consists of obtaining a steady-state solution of the equation of motion of the spin density matrix, which includes the effects due to the two radio-frequency fields and the relaxation in the system. A coordinate frame rotating at the angular frequency of the strong irradiating field is chosen for convenience. For the purpose of the present work, the relaxation part is included in the equation of motion under the two limiting cases of "strong" and "weak" collisions for the system. Double-resonance spectra were calculated separately within the framework of these two models for the collisions, and the results are compared with the experiments.

### THEORY

The assumption of the type of collisions in the system as either "weak" or "strong" enters into the density-matrix description of double resonance<sup>18-20</sup> through the correlation functions occurring in the relaxation part of the equation of motion. The distinction between the two models appears in the formalism in the equation

$$\frac{d\sigma^I}{dt} = -\text{Tr}_f \left\{ \int_{t_0}^t [\mathcal{H}C'^I(t), [\mathcal{H}C'^I(t-\tau), \lambda^I(t_0)\sigma^I(t)]] d\tau \right\}, \quad (1)$$

where  $\mathcal{H}C'^I$ ,  $\sigma^I$ , and  $\lambda^I$  are, respectively, the relaxation Hamiltonian, the density matrices of the spin and of the lattice parts in the interaction picture.  $\text{Tr}_f\{ \}$  represents a trace over all lattice states. This equation is practically the same as Eq. (66') of Ref. 3.

The procedure for further development of this equation in the strong-collision limit is given by Freed<sup>18</sup> in detail. In this model the lattice distribution is assumed to be the equilibrium distribution at the end of each collision. The time  $\tau$  between collisions or the correlation time is therefore independent of the transformation properties of the different interactions included in  $\mathcal{H}C'$ . With this assumption  $\sigma^I(t)$  is expressed parametrically in terms of  $t_0$  which is taken to be the time just after a collision.  $\lambda^I(t_0)$  is therefore replaced by the Boltzmann distribution, and the final equation is then obtained by weighting Eq. (1) with the probability that a collision has, in fact, taken place at the time  $t_0$ .<sup>18</sup>

The features of the weak-collision model are available in the theories of Oppenheim and Bloom,<sup>8,9</sup> and Needler and Opechowski.<sup>10</sup> The weak collisions are

characterized by the fact that the probabilities of transitions between the various lattice states are small per collision. The lattice, therefore, remains practically in thermal equilibrium all the time so that  $\lambda^I(t_0)$  in Eq. (1) can then be replaced by the Boltzmann distribution. Oppenheim and Bloom<sup>8</sup> have also shown that the correlation functions in this limit are exponential. The correlation times in these functions, however, depend on the transformation properties of the different interactions in  $\mathcal{H}C'$ .

In the application of this theory to the double-resonance problem there is an additional complication since the spin Hamiltonian is explicitly time-dependent.<sup>19</sup> This can be circumvented in the present case for both the above collision models by assuming "extreme narrowing" as in the case of liquids,<sup>3,18</sup> since the correlation times in the gases are of the order of  $10^{-11}$  sec.<sup>15</sup> In addition, for both these models, the fact that the spin density matrix  $\sigma(t)$  decays to the thermal-equilibrium value at the lattice temperature is to be introduced in the usual manner.<sup>3</sup>

By introducing into the general formalism<sup>18-20</sup> the conditions described in the above paragraphs it can be shown that the equation of motion of the spin density matrix describing the double resonance problem within the framework of strong- and weak-collision models is substantially of the same form as the familiar one used for liquids. In particular it is essential for the present discussion to note that the equation of motion for the two collision models has precisely the same form, with the important distinction that the correlation times for weak collisions depend on the transformation properties of the different interactions causing relaxation, while in the strong-collision limit they have no such dependence.

In the case of the HD molecule the lattice operators refer to the rotational degrees of freedom of the molecule. It is worthwhile noting in this connection that the collisions in which the rotational quantum number  $J$  of the molecule changes do not contribute effectively to the spin relaxation matrix elements since the rotational level spacings are larger than the inverse of correlation times of the system over a wide range of experimental conditions including the present.<sup>10,15</sup> This can be seen by substituting explicitly for the rotational level spacings and correlation times into the expressions like those given by Freed [Eq. (2.15)]. Practically all the contribution comes from collisions involving a change in the orientation of  $J$ , represented by the quantum number  $m_J$ . Only the matrix elements within each  $J$  manifold are, therefore, required to calculate the correlation functions. This fact can be used in conjunction with the Wigner-Eckart theorem<sup>21</sup> to re-express all the orientation-dependent parts of the relaxation Hamiltonian in terms of functions of rotational angular-momentum operators. This does not mean, however,

<sup>18</sup> B. D. Nageswara Rao, *Phys. Rev.* **137**, A467 (1965).

<sup>19</sup> A. Abragam, *Ref. 3*, Chap. XII.

<sup>20</sup> F. Bloch, *Phys. Rev.* **102**, 104 (1956).

<sup>21</sup> M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, New York, 1957), Chap. V.

that the situation is the same as if there were no collisions involving a change in  $J$  quantum number, since the total absence of such collisions restricts one to a separate correlation time of each kind for each  $J$  state, while if the  $J$  states change often each correlation time should be averaged over all the  $J$  states.

The interactions responsible for spin relaxation in HD are the spin-rotation interactions of the two nuclei, the mutual dipole-dipole interaction between them, and the nuclear electric-quadrupole interaction of the deuteron.<sup>6,14</sup> The spin-rotation interaction for a linear diatomic molecule is linear in the components of the rotational angular momentum which transforms like a vector. The parts involving rotation operators in the dipole-dipole and the electric-quadrupole interactions transform like components of a second-rank tensor (see Eq. 6). A separate correlation time can be proposed for each component of the vector- and tensor-type interactions. But as pointed out by Johnson and Waugh,<sup>14</sup> since the Larmor frequency of the rotational magnetic moment of HD is very small compared to the inverse of the correlation times involved, the direction of  $J$  remains practically unchanged between collisions and therefore the correlation times depend only on the rank of the interaction and not the components. The problem is therefore characterized by only two different correlation times.

The equation of motion of the spin density matrix  $\bar{\sigma}$ , for the double-resonance problem in HD, in a coordinate system rotating at the angular frequency  $-\omega_2 \mathbf{k}$  of the irradiating field, is thus given by

$$d\bar{\sigma}/dt = -i[\mathfrak{H}_0^R + \tilde{\mathfrak{H}}_1(t), \bar{\sigma}] - \Gamma(\bar{\sigma} - \sigma_0), \quad (2)$$

where operators in the rotating frame are identified by putting a tilde ( $\sim$ ) on top;  $\mathfrak{H}_0^R$  and  $\tilde{\mathfrak{H}}_1(t)$  are, respectively, the stationary and time-dependent parts of the spin Hamiltonian, expressed in angular-frequency units, in the rotating frame of reference; and  $\Gamma(\bar{\sigma} - \sigma_0)$  is the relaxation term. Equation (2) is identical with Eq. (32) of Ref. 18. The notation and definitions are also the same with one principal exception. The expression for  $J_{\alpha\beta\alpha'\beta'}$  involved in the matrix elements of  $\Gamma(\bar{\sigma} - \sigma_0)$  now becomes

$$J_{\alpha\beta\alpha'\beta'} = \sum_J \sum_{l,q} [P_J \tau_J^l / (2J+1)] \times (\sum_{m_J, m_J'} \langle m_J | F_l^{(q)} | m_J' \rangle |^2) \times \langle \alpha | A_l^{(q)} | \beta \rangle \langle \alpha' | A_l^{(q)} | \beta' \rangle, \quad (3)$$

where  $P_J$  is the weighting factor for the rotational states given by

$$P_J = \frac{(2J+1) \exp(-E_{J, m_J}/kT)}{\sum_J (2J+1) \exp(-E_{J, m_J}/kT)} \quad (4)$$

and  $\tau_J^l$  is the correlation time expressed as a function of  $J$  and the rank  $l$  of the interaction. The terms  $F_l^{(q)}$  and  $A_l^{(q)}$  are, respectively, the rotation and spin operators, expressed in irreducible form, contained in the re-

laxation Hamiltonian through the relation

$$\mathfrak{H}' = \sum_{l,q} F_l^{(q)} A_l^{(q)}, \quad (5)$$

such that  $F_l^{(q)} = F_l^{(-q)\dagger}$  and  $A_l^{(q)} = A_l^{(-q)\dagger}$ . For the HD molecule  $\mathfrak{H}'$  is given by<sup>6,14,15</sup>

$$\begin{aligned} \mathfrak{H}' = & C_H' [I_{zH} J_z + \frac{1}{2} (I_{+H} J_- + I_{-H} J_+)] \\ & + C_D' [I_{zD} J_z + \frac{1}{2} (I_{+D} J_- + I_{-D} J_+)] \\ & + \frac{3\gamma_H \gamma_D \hbar}{2r^3 (2J-1)(2J+3)} \\ & \times [\frac{2}{3} (3I_{zH} I_{zD} - \mathbf{I}_H \cdot \mathbf{I}_D) (3J_z^2 - J^2) \\ & + (I_{+H} I_{zD} + I_{zH} I_{+D}) (J_+ J_z + J_z J_+) \\ & + (I_{-H} I_{zD} + I_{zH} I_{-D}) (J_- J_z + J_z J_-) \\ & + I_{+H} I_{+D} J_+^2 + I_{-H} I_{-D} J_-^2] \\ & - \frac{3eQq}{8\hbar (2J-1)(2J+3)} [\frac{2}{3} (3I_{zD}^2 - I_D^2) (3J_z^2 - J^2) \\ & + (I_{+D} I_{zD} + I_{zD} I_{+D}) (J_+ J_z + J_z J_+) \\ & + (I_{-D} I_{zD} + I_{zD} I_{-D}) (J_- J_z + J_z J_-) \\ & + I_{+D}^2 J_+^2 + I_{-D}^2 J_-^2], \quad (6) \end{aligned}$$

where  $C_i'$ ,  $I_i$ , and  $\gamma_i$  are the spin-rotation interaction constant, spin angular momentum, and magnetogyric ratio of the nuclei  $i = H, D$ ;  $eQq$  is the quadrupole coupling constant of deuteron in HD; and  $r$  is the internuclear distance between H and D. Introducing the modifications embodied in Eqs. (3) through (6) into Eq. (2), we can obtain a steady-state solution for the spin density matrix  $\bar{\sigma}$  in a manner similar to that described earlier.<sup>18</sup> The form of Eqs. (2) and (3) is exactly the same for strong- and weak-collision models. The distinction appears exclusively through the correlation times  $\tau_J^l$  which should be dependent on  $l$  for weak collisions and independent of  $l$  for strong collisions. The dependence on  $J$  is closely related to the question of whether the number of collisions involving a change in  $J$  is significant.

Finally, it may be noted from Eq. (6) that the components of the rotational operators are identical in the corresponding terms of the two spin-rotation interactions ( $l=1$ ) and of the dipole-dipole and quadrupole interactions ( $l=2$ ). Using this and Eq. (3) it can be seen that the cross products between terms with the same  $l$  and  $q$  but belonging to two different interactions, do not vanish. These products are usually disregarded in calculations of relaxation times.<sup>14,15</sup> There is no obvious physical reason why these terms should be neglected. The importance of these cross terms is determined by the relative strengths of the interactions involved and is, in general, different for the various  $J_{\alpha\beta\alpha'\beta'}$  elements. These terms are retained in the present

calculation and are found to make an appreciable difference in the final results.

### EXPERIMENTAL

A sample containing HD and CO<sub>2</sub> at partial pressures of approximately 10 and 20 atm, respectively, was used in the experiments.<sup>22</sup> Carbon dioxide was added to HD, in accordance with the results of Johnson and Waugh,<sup>14</sup> to shorten rotational correlation times and thereby lengthen the spin relaxation time and narrow the resonances in the high-resolution spectrum. Frequency-sweep double-resonance spectra were obtained with a field-frequency lock system using a spin decoupler,<sup>23</sup> in conjunction with a Varian V-4300 high-resolution NMR spectrometer. Since the reference signal required for locking the magnetic field is not available in the sample, it was provided by a thin capillary containing tetramethylsilane with a coil wound around it, introduced close to the insert containing the receiver coil in the Varian probe. The signal picked up by the coil was fed to the receiver through a coupling network. This arrangement provided a short-term stability comparable to schemes using internal standards, though the long-term stability is somewhat less since the sample and the standard are spatially separated.<sup>24</sup>

Double-resonance experiments were performed by observing the proton resonance spectrum while irradiating either one of the proton transitions or the deuteron transitions. Irradiation of the proton transitions was obtained by an audio-frequency modulation scheme.<sup>23</sup> Irradiation of the deuteron transitions was done with a high-level, crystal-controlled oscillator of adjustable output voltage and variable frequency over a range of about 500 cps. The NMR probe was tuned to both the proton and deuteron frequencies (about 60 and 9.2 Mc/sec, respectively) by adding a coupling circuit described earlier.<sup>25</sup> The frequencies of the deuteron transitions were located by changing the irradiating frequency and observing the mirror-image spectra<sup>26</sup> for frequencies symmetrical with respect to the center of the deuteron spectrum. All the experiments were done at room temperature.

### RESULTS

The proton resonance spectrum of HD consists of a triplet of equal intensity as shown in Fig. 1. The multi-

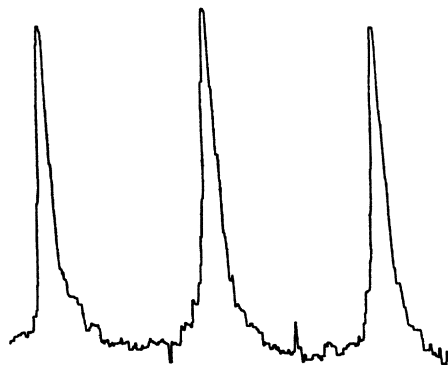


FIG. 1. The proton single-resonance spectrum of HD. The triplet arises from a spin-spin coupling constant of  $43.2 \pm 0.5$  cps between the nuclei.

plet separation gives directly the value of the spin-spin coupling constant  $J_{HD} = 43.2 \pm 0.5$  cps, in good agreement with the previously determined values.<sup>27,28</sup> The full linewidth at half-height of the resonances is about 3.5 cps. A proton-proton double-resonance spectrum obtained by irradiating near the low-field single-resonance transition is shown in Fig. 2, and in Figs. 3 and 4 are shown proton resonance spectra when the irradiating frequency is set close to the low-field deuteron resonance for two different values of the strength of irradiation. The asymmetry in the intensities in the proton-deuteron double-resonance spectra shows that the relaxation effects are important. It may also be noted that the proton-deuteron double-resonance spectra show further splitting of the single-resonance transitions, but no new signals are observed in the proton-proton resonance spectra. This occurs because

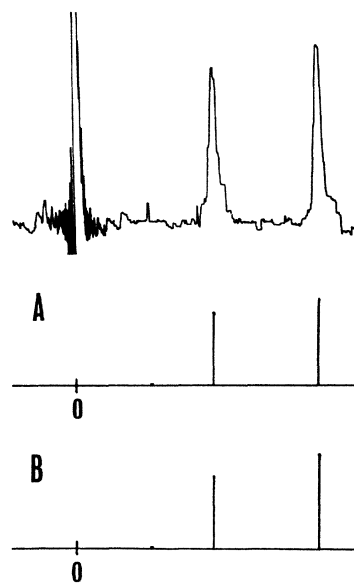


FIG. 2. The proton-proton double-resonance spectrum obtained with the parameters  $A_H = 43.2$  cps and  $\nu_{2H} = 27.9$  cps. The theoretical spectra A and B refer to the results of strong- and weak-collision models, respectively.

<sup>22</sup> We are indebted to Dr. K. Kuhlmann and Professor J. D. Baldeschwieler for giving us this sample which they prepared earlier.

<sup>23</sup> J. H. Noggle, *Rev. Sci. Instr.* **35**, 1166 (1964).

<sup>24</sup> The details of the field-locking scheme using an external reference along with a preliminary account of the research in the present paper were reported at the Sixth Experimental NMR Conference held at the Mellon Institute, Pittsburgh, Pennsylvania, 1965 (unpublished).

<sup>25</sup> R. C. Hopkins, *Rev. Sci. Instr.* **35**, 1495 (1964).

<sup>26</sup> J. M. Anderson and J. D. Baldeschwieler, *J. Chem. Phys.* **37**, 39 (1962).

<sup>27</sup> H. Y. Carr and E. M. Purcell, *Phys. Rev.* **88**, 415 (1952).

<sup>28</sup> T. F. Wimmert, *Phys. Rev.* **91**, A476 (1953).

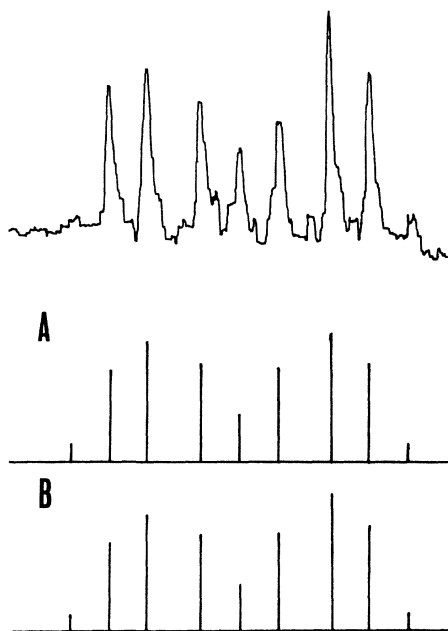


FIG. 3. The proton-deuteron double-resonance spectrum obtained with parameters  $A_D = -24.0$  cps, and  $\nu_{2D} = 13.6$  cps. The theoretical spectra A and B refer to the results of strong- and weak-collision models, respectively.

the irradiated transitions have energy levels in common with all the observed transitions in the former case while in the latter case there are no such common energy levels.<sup>29</sup> The stationary part of the spin Hamiltonian in the rotating frame  $\mathcal{H}_0^R$  can be readily diagonalized for all the above cases and the frequency offset  $A_i$  (difference between irradiating frequency and

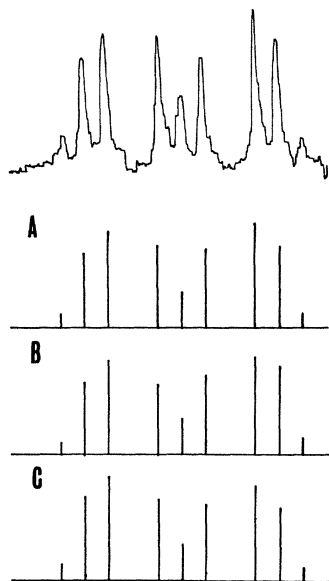


FIG. 4. The proton-deuteron double-resonance spectrum obtained with parameters  $A_D = -24.0$  cps, and  $\nu_{2D} = 11.3$  cps. The theoretical spectra A and B refer to the results of strong- and weak-collision models, respectively. Spectrum C is the result of calculations done by discarding the cross terms between different relaxation mechanisms.

<sup>29</sup> W. A. Anderson and R. Freeman, *J. Chem. Phys.* **37**, 85 (1962).

nuclear Larmor frequency) and strength of irradiation  $\nu_i$  involved in each spectrum can be determined directly from the observed frequencies. These values are  $A_H = 43.2$  cps,  $\nu_{2H} = 27.9$  cps;  $A_D = -24.0$  cps,  $\nu_{2D} = 13.6$  cps; and  $A_D = -24.0$  cps,  $\nu_{2D} = 11.3$  cps for the spectra in Figs. 2, 3, and 4, respectively.

All the interaction constants involved in Eq. (6) have been determined accurately for free HD molecules by molecular-beam experiments.<sup>30</sup> The data required for a complete calculation of the spectra with the exception of the correlation times are thus known. It may be noted that only the relative values and not the absolute values of correlation times are important for the calculation. At room temperature, rotational levels of HD up to  $J = 4$  are appreciably populated. The collisions involving a change in  $J$  should therefore be considered before proceeding with the calculation. As pointed out by Bloom,<sup>15</sup> on the basis of the intermolecular interactions and energy-conservation considerations, the most probable collisions for which the value of  $J$  of a HD molecule changes are those of the resonant type where molecules with rotational angular momenta differing by one unit collide and interchange their energies. For our present sample, a simple calculation<sup>31</sup> of collision frequencies between different molecules shows that the resonant collisions are only about 12% of the total number of collisions involving HD molecules. The collisions involving a change of  $J$  are thus not very significant for the present problem. Assuming a weak-collision model and absence of collisions involving changes in  $J$ , Bloom *et al.*<sup>32</sup> derived that the  $J$  dependence of  $\tau_J^1$  and  $\tau_J^2$  is given by

$$\tau_J^1 \propto (2J-1)(2J+3), \quad (7)$$

$$\tau_J^2 \propto \frac{(2J-1)^2(2J+3)^2}{3(4J^2+4J-7)}. \quad (8)$$

The calculations for the weak-collision model were made using Eqs. (7) and (8). There are no formulas available if the collisions involving changes in  $J$  are important. For strong collisions one has  $\tau_J^1 = \tau_J^2$ . Since the collisions involving changes in  $J$  are not very numerous, the strong-collision model in the present case refers primarily to collisions involving a change in  $m_J$  within a  $J$  manifold and for this reason a dependence of  $\tau$  on  $J$  could be considered. But the basic model proposed for strong collisions,<sup>33</sup> that the phases of lattice states are completely randomized at the end of each collision, should perhaps preclude any dependence of  $\tau$

<sup>30</sup> W. E. Quinn, J. M. Baker, J. T. LaTourrette, and N. F. Ramsey, *Phys. Rev.* **112**, 1929 (1958).

<sup>31</sup> S. Chapman and T. G. Cowling, *The Mathematical Theory of Non-Uniform Gases* (Cambridge University Press, Cambridge, England, 1960).

<sup>32</sup> M. Bloom, I. Oppenheim, M. Lipsicas, C. G. Wade, and C. F. Yarnell, *J. Chem. Phys.* **43**, 1036 (1965).

<sup>33</sup> J. H. Van Vleck and V. W. Weisskopf, *Rev. Mod. Phys.* **17**, 227 (1945).

on these quantum numbers. The strong-collision calculations were, therefore, made by setting  $\tau_{J^1} = \tau_{J^2} = \tau$ .

The computations were done on an IBM-7094 computer. It was not possible, however, to use Bloch's approximation,<sup>18,20</sup> discussed earlier, to simplify the calculations in every case, since the linewidths in the spectrum are larger than those encountered in usual high-resolution NMR spectra. But it was possible to make a partial approximation for the problem<sup>18</sup> which reduced the total number of simultaneous equations required for a complete solution to 12.

The theoretical double-resonance spectra for strong- and weak-collision models are denoted by (A) and (B), respectively, in Figs. 2, 3, and 4. A good comparison with the observed spectra could only be made by considering a number of experimental spectra and comparing their average features with the theoretical calculations. This is mainly because the signals involved are weak, requiring operation of the spectrometer near the limiting conditions with the attendant factors of slight drift and instability in the experiment. Such a comparison with the observed spectra shows that the results of the strong-collision model describe the proton-deuteron experiments very closely and significantly better than the weak-collision results. (Figures 3 and 4; note in particular the doublet close to the center for which the observed asymmetry is obtained in the (A) spectra and is reversed in the (B) spectra.) It is difficult to distinguish between the results of the two models in the proton-proton double-resonance spectra in Fig. 2, since there are only two transitions observed. It may be noted that in the actual calculation the difference between the two models only changes the relative contribution of interactions with  $l=1$  and  $l=2$  to the complete relaxation matrix given by terms like  $J_{\alpha\beta\alpha'\beta'}$  in Eq. (3). In the present case, unfortunately, the predominant contribution comes from  $l=1$  mechanisms, particularly for proton relaxation. This is the reason the results for the two collision models do not differ as strikingly as one might expect from the principle of the method, even for the proton-deuteron experiments. The weak-collision calculation is based on the assump-

tion of the particular  $J$  dependence of  $\tau_{J^l}$  given by Eqs. (7) and (8). An empirical fitting of the observed spectrum to a set of correlation times for each  $J$  state is not practical since there are too many parameters arising from the various  $J$  states. Furthermore such a fitting seems hardly worthwhile as it does not explicitly signify the applicability of any model. Based on these considerations it is only possible to say that the experiments are described better by the strong-collision model than by the weak-collision model. The conclusion that the collisions in HD are close to being "strong" is in agreement with that reached by Hardy<sup>15</sup> from relaxation-time measurements.

In order to test the importance of cross terms in the correlation functions arising from components of different interactions transforming similarly, the strong-collision calculations were repeated for the case shown in Fig. 3, by discarding these terms. The results are shown in Fig. 3(C). It may be seen that the theoretical intensities in the spectrum are different from those in Fig. 3(A), where the cross terms are retained. The cross terms in the correlation functions are thus apparently significant in a general analysis like the present one in which a variety of matrix elements of the type  $J_{\alpha\beta\alpha'\beta'}$  are required, although they may not be important for computing some particular types of matrix elements.

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