

FORMATION AND BREAKUP RATES OF RbXe VAN DER WAALS MOLECULES IN He AND N₂ GAS

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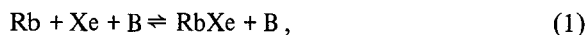
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Received 6 June 1983; in final form 17 July 1983

The efficiency of He, as a third body, in the formation and breakup of RbXe van der Waals molecules has been measured. The formation and breakup rates of RbXe molecules are the same if a given pressure of nitrogen gas is replaced by 1.6 times more helium gas to serve as a third body. The nuclear spin relaxation of ¹²⁹Xe in ⁸⁷Rb is described by a universal function of the third-body pressure measured in units of a characteristic pressure P_0 .

The relaxation rates of spin polarized alkali atoms in the heavy rare gases, Ar, Kr and Xe are known to be dominated by spin interactions in loosely bound alkali-rare-gas van der Waals molecules, as was first pointed out by Bouchiat et al. [1]. Recent work [2,3] has shown that the relaxation rate of nuclear spin polarized Xe gas in alkali vapors is also dominated by the same van der Waals molecules. The van der Waals molecules are formed in three-body collisions in which the third body might be a rare-gas atom of the same species which is bound into the molecules [1,4], or it might be a different atom or non-reactive molecule [2,3] like N₂. In this paper we present the results of the first experimental comparison of the efficiencies of two different third bodies, He atoms and N₂ molecules for forming or breaking up RbXe van der Waals molecules.

Alkali-rare-gas van der Waals molecules are formed by reactions of the type



where B represents a third-body atom or molecule. For given atomic number densities of [Rb] and [Xe] the molecular number density [RbXe] should be independent of the nature of the third body if the system pressure is not too high. The densities should be related by the law of mass action,

$$K = [\text{RbXe}]/[\text{Rb}][\text{Xe}] = 9.4 \times 10^{-22} \text{ cm}^3, \quad (2)$$

where the value of K in (2) was measured at $\approx 70^\circ\text{C}$ in ref. [3]. It is interesting to note that (2) implies that at a characteristic alkali density [Rb] = 10^{12} cm^{-3} only one Xe atom in 10^9 is bound into a RbXe van der Waals molecule. Nevertheless, most of the nuclear spin relaxation of ¹²⁹Xe atoms in Rb vapor occurs in van der Waals molecules. Binary collisions between Rb and Xe atoms make only a minor contribution to the relaxation [3].

The spin relaxation rates of rare-gas nuclei or of alkali electronic spins depend on the formation and breakup rates of the RbXe molecules and not on the equilibrium constant (2) alone. In ref. [3] it was shown that the alkali-induced nuclear spin relaxation rate of a ¹²⁹Xe atom, θ_0^{-1} , is

$$\theta_0^{-1} = p_k/T_k, \quad (3)$$

where $1/T_k$ is the mean rate of formation of RbXe molecules per Xe atom and p_k is the probability that the nuclear spin is destroyed during the molecular lifetime. The electronic spin S of the alkali atom in the molecule is coupled to the alkali nuclear spin I , to the rotational angular momentum N of the RbXe molecule and to the nuclear spin K of the ¹²⁹Xe nucleus by the hamiltonian [5]

$$H = A I \cdot S + \gamma N \cdot S + \alpha K \cdot S. \quad (4)$$

As discussed in ref. [3] the hamiltonian (4) could account for all data on spin relaxation of alkali atoms or

rare-gas nuclei known at that time. The hamiltonian (4) implies that the spin destruction probability, to lowest order in x^{-2} , is

$$p_k = \frac{1}{6}(1-x^{-2}) \frac{(\phi/2x)^2}{1+(\phi/2x)^2} + \frac{1}{3}(1-\frac{3}{2}x^{-2}) \frac{(\phi/4x)^2}{1+(\phi/4x)^2} \\ + 2x^{-2} \frac{(\phi/4)^2}{1+(\phi/4)^2} + \frac{1}{12}(1-x^{-2}) \frac{(\phi/4x^2)^2}{1+(\phi/4x^2)^2} \\ + \frac{1}{12}(1-3x^{-2}) \frac{(3\phi/4x^2)^2}{1+(3\phi/4x^2)^2}. \quad (5)$$

Physically eq. (5) describes the rotation of the xenon nuclear spins about the vector N for the three possible projection of $S + S$ along N , i.e. $|m_S + m_I| = 2, 1$ or 0 with statistical weights $\frac{1}{6}, \frac{1}{3}$ and $\frac{1}{6} = \frac{1}{12} + \frac{1}{12}$ respectively. Small correction terms of order x^{-2} are also included. A more detailed description of eq. (5) can be found in ref. [3]. The phase angle

$$\phi = \gamma N \tau / h \quad (6)$$

is the product of the spin-rotation interaction constant γN of (4) and the mean molecular lifetime τ . The expansion parameter

$$x = \gamma N / \alpha \quad (7)$$

is the ratio of the (root mean square) spin-rotation interaction constant γN and the spin exchange coupling constant α . For $^{87}\text{Rb } ^{129}\text{Xe}$ molecules the value of $x = 4.1$ was measured in ref. [6].

Under the experimental conditions of interest for this work the molecular lifetime τ is inversely proportional to the third-body pressure and the phase evolution angle ϕ of (6) may therefore be written as

$$\phi = P_0 / P, \quad (8)$$

where P_0 is that value of the third-body pressure for which the phase angle ϕ is unity. The formation rate T_k^{-1} of (3) and the breakup rate τ^{-1} of (6) must be related by

$$[\text{RbXe}] \tau^{-1} = [\text{Xe}] T_k^{-1}, \quad (9)$$

when reaction (1) has driven the system to chemical equilibrium. Combining (9), (8) and (6) with (3) we conclude that the nuclear spin relaxation rate of the ^{129}Xe is

$$\theta_0^{-1} = [\text{Rb}] K (\gamma N / h) \phi^{-1} p_k^{(\phi)}. \quad (10)$$

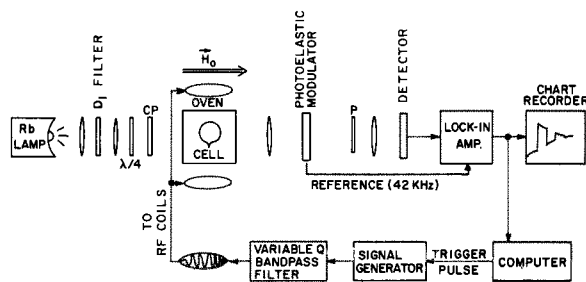


Fig. 1. A schematic of the apparatus.

Thus, from (10) we expect to find that the molecule-induced nuclear spin relaxation of ^{129}Xe will depend on the third-body pressure through the *universal function* $\phi^{-1} p_k(\phi)$. The other factors in (10) are independent of the nature of the third body. The experiments described below show that the measured relaxation rates of ^{129}Xe in N_2 and He gases are in good agreement with the prediction (10).

The experimental apparatus is schematically shown in fig. 1. The cell is pyrex sphere 30 mm in diameter. The inside walls are treated with a commercial silicone coating agent (Surfrasil)[†]. The coating process and its advantages have been previously discussed [7]. The coated cells are filled with ≈ 0.5 Torr Xe (70% ^{129}Xe), a few droplets of ^{87}Rb metal, an appropriate amount of He and are sealed off. A dc magnetic field (≈ 5 G) which is produced by the large coils defines the Larmor frequencies of ^{87}Rb and ^{129}Xe , and lessens the sensitivity of the system to stray magnetic fields. The cell is heated by a stream of hot air and the mixture in it is optically pumped by a ^{87}Rb vapor resonance lamp using a circular polarizer (CP) and a filter which transmits the 794.76 nm (D1) line. During the probe phase of the experiment the circular polarizer is removed and the small amount of elliptical polarization introduced in the unpolarized light by the polarized ^{87}Rb atoms is detected with a photoelastic modulator [7]. The signal is proportional to the number density of the spin-polarized ^{129}Xe nuclei since the short-lived (≈ 1 ms) polarized ^{87}Rb atoms are produced by spin exchange with the xenon. Small amounts of stray elliptical polarization caused by the lamp it-

[†] Surfrasil is manufactured by Pierce Chemical company, Rockford, Illinois 61105, USA.

self and by the optical components are initially compensated by a rotatable $\lambda/4$ plate. The stray components of the elliptical polarization are temperature sensitive. This leads to a slow, unpredictable drift in the elliptical background polarization during the long ($\approx \frac{1}{2}$ h) relaxation time. To compensate for the slow drift we perform adiabatic rapid passage [9], i.e. we periodically invert the ^{129}Xe nuclear polarization with a chirped audio-frequency magnetic field which is applied to the small coils. The frequency is swept from 3 to 7 kHz through the ^{129}Xe magnetic resonance of 5 kHz. The xenon polarization is determined by subtracting the average signals during the five second intervals before and after an inversion. This procedure is equivalent to transforming the signal power to higher frequencies and it eliminates noise frequencies with periods longer than ten seconds. An Apple II plus computer controls the inversion rates and performs on-line data processing. The signal amplitude is given by $A(t) = A(0)(1 - \epsilon)^n \exp(-t/\theta)$, where ϵ is the decay per inversion, n is the number of inversions and θ is the ^{129}Xe relaxation time. Variation of the interval between consecutive inversions permits the

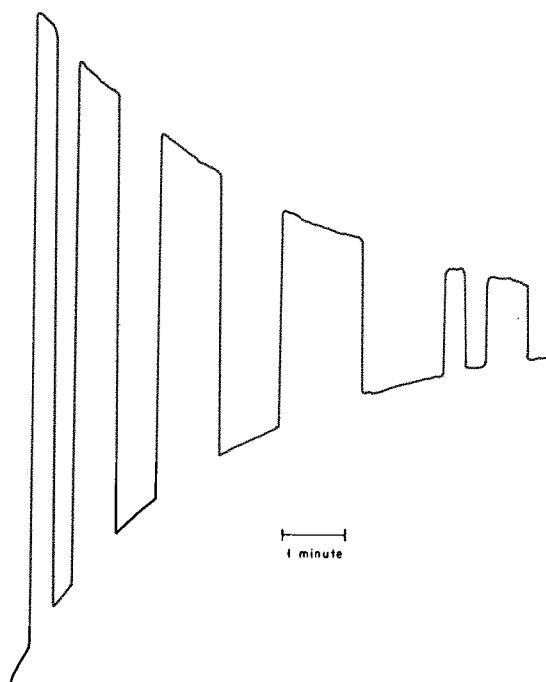


Fig. 2. ^{129}Xe decay curve. $P(\text{He}) = 48.5$ Torr, $[\text{Rb}] = 2.12 \times 10^{11} \text{ cm}^{-3}$.

determination of both θ and ϵ from the decay curve. Independent measurements of θ under the same conditions have a variance from their mean of $\approx 5\%$. A typical decay curve is presented in fig. 2. The decay rate of the ^{129}Xe nuclear polarization θ^{-1} results from the combined effects of spin exchange θ_0^{-1} and wall relaxation rate T_w^{-1} ,

$$\theta^{-1} = \theta_0^{-1} + T_w^{-1} = C[\text{Rb}] + T_w^{-1},$$

where C and T_w^{-1} are temperature-independent constants. The quantities C and T_w^{-1} are determined by measuring θ^{-1} at various temperatures as shown in fig. 3. The Rb density is deduced from the measurement of the cell temperature with a non-magnetic thermocouple and by using Smithells' formula for temperature dependence of the saturated vapor pressure of rubidium [10]. The effect of the third body is determined by measurement of θ^{-1} for cells with different number densities of He (denoted by the filling pressure at room temperature).

The relaxation data for ^{129}Xe in ^{87}Rb vapor are summarized in fig. 4 for a Rb density of 10^{12} cm^{-3} (85.3°C). We have included the results obtained in this work for He as a third body along with previously published data for N_2 as a third body [2,3]. The characteristic pressure for helium is

$$P_0(\text{He}) = 175 \text{ Torr},$$

while the characteristic pressure for N_2 was

$$P_0(\text{N}_2) = 107 \text{ Torr}.$$

It is not surprising that the He atoms, which are very unpolarizable, are required in greater amounts than

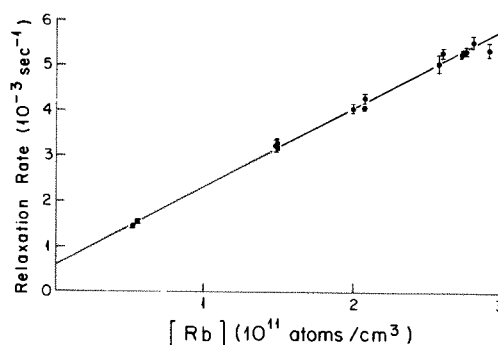


Fig. 3. ^{129}Xe decay rates as a function of Rb density. $P(\text{He}) = 48.5$ Torr.

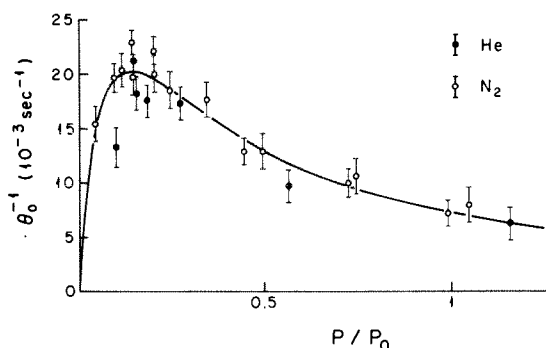


Fig. 4. Combined He-N₂ rate curve.

N₂ molecules to produce the same third-body effects. Both the He and the N₂ data are well described by (10), which is the solid curve in fig. 4, if the dissociation equilibrium constant is given by (2) and the spin-rotation interaction constant is

$$\gamma N/h = 120 \text{ MHz.}$$

The only other information on three-body rates for the RbXe system was obtained by Bouchiat et al. [4] in their studies of Rb spin relaxation. Converting their P^* to our P_0 by the relation $P_0 = (2I + 1)P^* = 4P^*$ we find

$$23 \text{ Torr} \lesssim P_0(\text{Xe}) \lesssim 40 \text{ Torr.}$$

The large uncertainty is due to the limitation of the measurements of ref. [4] to rather low Xe pressures.

In conclusion we have shown that the Rb-induced

nuclear spin relaxation of ¹²⁹Xe is described by a universal function of the third-body pressure, measured in units of the characteristic pressure P_0 . Other alkali-rare-gas pairs should obey a similar law, which will depend on the interaction constants of a hamiltonian similar to (4).

This work was supported by the US Air Force Office of Scientific Research under Grant No. AFOSR-81-01048.

References

- [1] C.C. Bouchiat, M.A. Bouchiat and L.C.L. Pottier, Phys. Rev. 181 (1969) 144.
- [2] C.H. Volk, T.M. Kwon and J.G. Mark, Phys. Rev. A21 (1980) 1549.
- [3] N.D. Bhaskar, W. Happer, M. Larsson and X. Zeng, Phys. Rev. Letters 50 (1983) 105.
- [4] M.A. Bouchiat, J. Brosset and L.C. Pottier, J. Chem. Phys. 56 (1972) 3703.
- [5] R.S. Frosch and H.M. Foley, Phys. Rev. 88 (1952) 1337.
- [6] N.D. Bhaskar, W. Happer and T. McClelland, Phys. Rev. Letters 49 (1982) 25.
- [7] X. Zeng, E. Miron, V.A. van Wijngaarden, D. Schreiber and W. Happer, Phys. Letters 96A (1983) 191.
- [8] J. Kemp, J. Opt. Soc. Am. 53 (1969) 950.
- [9] C.P. Slichter, Principles of magnetic resonance (Springer, Berlin, 1978) p.26.
- [10] C.J. Smithells, Metals reference handbook, Vol. 2 (Butterworths, London, 1962) p.655.