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Nuclear Magnetic Resonance of Diatomic Alkali Molecules in Optically Pumped Alkali Vapors*

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NMR signals from diatomic alkali molecules have been observed in optically pumped cesium and rubidium vapors. The nuclear relaxation times were found to be strongly dependent on the temperature and buffer-gas pressure. The relaxation time seems to be determined by at least two and possibly three major factors: motional narrowing of the molecular hyperfine structure, breakup of the diatomic molecules by collisions with buffer-gas atoms, and possibly chemical exchange of free atoms with atoms bound in the molecules.

Recently, Nienstadt *et al.*[1] have used the charge-exchange method of Mitchell and Fortson[2] to make precision measurements of the Cs$^+$ NMR frequency in optically pumped cesium vapor. During the course of this work Nienstadt *et al.*[1] noticed that NMR signals could still be observed even when no Cs$^+$ ions were intentionally produced in the vapor. They remarked that they "do not exclude the possibility that it [the signal] is associated with NMR in the Cs$_2$ molecule." We have observed similar NMR signals in optically pumped cesium and rubidium, and we present data which indicate that the signals do indeed originate in diatomic alkali molecules. The behavior of the molecules is strongly affected by the temperature and buffer-gas pressure, and these experiments afford a unique and simple way to observe simple gas-phase chemical reaction rates for a system in thermal equilibrium. These seem to be the first measurement of the formation and breakup rates of alkali molecules. The molecules also represent a new factor which must be taken into consideration when designing miniature optically pumped devices for operation at high temperature.[3]

Our data were obtained with the apparatus sketched in Fig. 1. Cesium metal was distilled

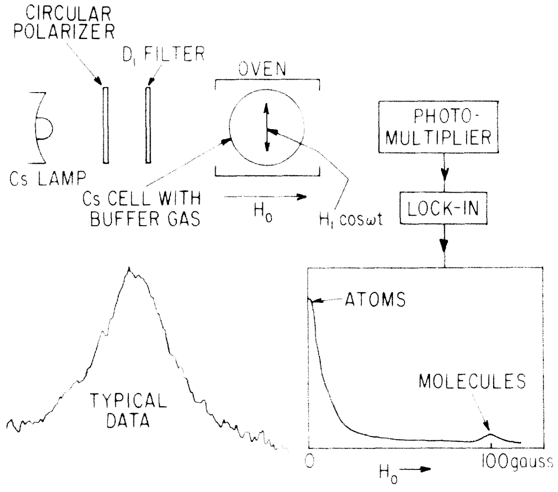

FIG. 1. Schematic diagram of the experimental arrangement and sketches of typical data.

into cylindrical Pyrex absorption cells, 5 cm in diameter and 1 cm in height. Various amounts of inert gas were introduced into these cells and the room-temperature (~22°C) pressure was measured before sealoff. The cells were placed in an oven, which controlled the temperature and hence the pressure of the saturated cesium vapor. The cells were optically pumped with circularly polarized D_1 (8943 Å) resonance radiation from a cesium lamp, and the transmitted pumping light was monitored with a photomultiplier tube. A large rf field with a peak amplitude of as much as 10 G and a frequency of 55 kHz was applied to the cells. The rf field was square-wave modulated on and off at 13 Hz, and the synchronous component of the transmitted light intensity was detected with a lock-in amplifier and displayed on a chart recorder.

A static magnetic field H_0 was swept from zero to several hundred gauss and signals of the type sketched in Fig. 1 were recorded. The large signal near zero magnetic field was presumably due to magnetic resonance of the cesium atoms, although the rf field amplitude was so large and the frequency so low that it is clear that the conventional Bloch solutions for the magnetic-resonance line shape need some revision to apply to our conditions. At a field of about 100 G a second resonance was usually seen. The amplitude of this high-field resonance seldom exceeded 5% of the amplitude of the low-field atomic resonance, and the shape of the high-field resonance was slightly distorted at higher rf powers by the shoulder of the low-field resonance. When small corrections were made for this distortion, it was found that the high-field resonance curve could be fitted very well by a Lorentzian curve,

$$S = \frac{\omega_1^2}{\gamma^2 + \omega_1^2 + (\omega - \omega_0)^2}. \qquad (1)$$

The resonance frequency ω_0 was found to be equal to the cesium NMR frequency

$$\omega_0 = 2\pi(558.5\ \mathrm{Hz/G})H_0. \qquad (2)$$

Small Bloch-Siegert[4] shifts of ω_0 could be observed at higher rf powers. The nutational frequency ω_1 was proportional to the amplitude of the rf field, which was monitored with a pickup loop near the cesium absorption cell. The residual width γ of the curve can be interpreted as the inverse of the transverse relaxation time τ of the nuclear spins.

A typical recording of a high-field resonance is sketched in Fig. 1. By obtaining magnetic resonance curves for a series of rf powers and extrapolating to determine γ, we were able to obtain data that are summarized in Fig. 2 for the dependence of τ on the buffer-gas pressure and on the temperature T of the saturated cesium vapor.

The two most likely species which could be responsible for our NMR signals are Cs^+ ions and diatomic cesium molecules. Although Cs^+ ions can be produced in optically pumped alkali vapors and their NMR signals can be readily observed,[1,2,5] there is no obvious source of Cs^+ ions in our work, and in thermal equilibirum the number density $[Cs^+]$ of Cs^+ ions is completely negligible compared to the number density $[Cs]$ of neutral cesium atoms,

$$[Cs^+]/[Cs] \simeq 10^{-25} \text{ at } 350°K. \qquad (3)$$

Furthermore, if the signals did originate from Cs^+ ions, there is no apparent mechanism which could account for the large broadening of the NMR resonances by the buffer gas. On the other hand, the behavior of the NMR signals can be readily understood if it is assumed that they originate in Cs_2 molecules. Although the molecular number density $[Cs_2]$ is a small fraction of the atomic number density,

$$[Cs_2]/[Cs] \simeq 5\times10^{-4} \text{ at } 350°K,$$

the rate of transfer of angular momentum between the atoms and molecules is still sufficient for the Cs_2 molecules to have an appreciable in-

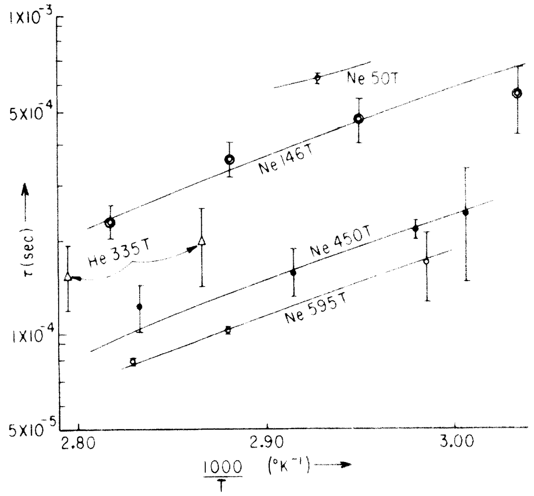

FIG. 2. Relaxation time of nuclear spins in Cs_2 as a function of temperature and the pressure of buffer gas. The curves are fits to the data based on the rate constants given in the text.

fluence on the atomic spin polarization.

The most striking feature of the data of Fig. 2 is the decrease of the relaxation time with increasing pressure and increasing temperature. This behavior can be understood most simply by assuming that the molecules are being broken up into atoms by the reaction

$$\mathrm{Cs}_2+\mathrm{Ne}\rightarrow\mathrm{Cs}+\mathrm{Cs}+\mathrm{Ne}. \tag{4}$$

Of course the inverse of (4), three-body association of cesium atoms into molecules, must also occur. Since the mean thermal energy of the neon atoms (~0.03 eV) is much smaller than the dissociation energy[6] (0.45 eV) of the cesium molecules, one would expect that only a small fraction of the collisions between Cs_2 and the buffer-gas atoms would lead to molecular dissociation. One would also expect the rate for the process (4) to be strongly temperature dependent, and to be characterized by an activation energy on the order of the molecular dissociation energy. Indeed, we find that the high-pressure data of Fig. 2 can be fitted very well by assuming that the rate for the process (4) is

$$1/\tau_g=\langle v\sigma\rangle_g e^{-4520/T}[\mathrm{Ne}], \tag{5}$$

where T is the absolute temperature, [Ne] is the number density of neon atoms, and the rate constant

$$\langle v\sigma\rangle_g\simeq 2\times10^{-10}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}. \tag{6}$$

The characteristic temperature, 4520°K, corresponds to an activation energy of 0.39 eV, which is reasonably close to the 0.45-eV dissociation energy[6] of Cs_2.

Another important experimental fact is the absence of any hyperfine structure (hfs) of the NMR signals. The diatomic alkali molecules are known to have a fairly large hfs due to the electrostatic interaction between the nuclear quadrupole moment Q and the electric field gradient q produced by the atomic electrons. Logan, Coté, and Kusch[7] find $eqQ/h=230$ kHz for $^{133}\mathrm{Cs}_2$ and $eqQ/h=1100$ kHz for $^{85}\mathrm{Rb}_2$. Because of the rapid reorientation of the rotational angular momentum J of the molecule due to collisions with the buffer-gas atoms, there should be a pronounced motional narrowing of the hfs, and the quadrupole interaction should manifest itself by causing the nuclear spins to relax at a rate[8]

$$\frac{1}{\tau_Q}=\frac{3}{40}\frac{2I+3}{I^2(2I-1)}\left(\frac{eqQ}{\hbar}\right)^2\tau_J, \tag{7}$$

where I is the nuclear spin and τ_J is the characteristic time for reorientation of J. We expect τ_J^{-1} to be proportional to the buffer-gas pressure, i.e.,

$$1/\tau_J=\langle v\sigma\rangle_J[\mathrm{Ne}]. \tag{8}$$

In contrast to molecular breakup (4), for which the electronic and nuclear spins should be conserved, the quadrupolar relaxation (7) represents a loss of nuclear-spin angular momentum to translational and rotational angular momentum of the molecules and buffer-gas atoms. Because of the factor τ_J in (7), we expect the quadrupolar relaxation rate to vary inversely as the buffer-gas pressure. The diffusion rate of the molecules to the cell walls also varies inversely with the pressure. However, the diffusion rates at 1 atm should not exceed 3 sec^{-1}, and the diffusion rates were therefore too small to have had a noticeable influence on the rates measured in this work.

Before concluding our discussion of quadrupolar relaxation let us note that a third process, chemical exchange, may also contribute to the NMR linewidth:

$$\mathrm{Cs}(1)\mathrm{Cs}(2)+\mathrm{Cs}(3)\rightarrow\mathrm{Cs}(1)+\mathrm{Cs}(2)\mathrm{Cs}(3). \tag{9}$$

Although chemical exchange is known to occur at a very slow rate in hydrogen and deuterium,[9] recent experiments by Whitehead and Grice[10] indicate that the chemical-exchange rates in the alkali atoms are quite fast and thermal-energy cross sections for the process (9) are on the order of 10^{-14} cm^2. Although we expect that chemical exchange will conserve the electronic and nuclear spins of the reactants in (9), the exchange collisions will contribute an amount $1/\tau_{ce}$ to the relaxation rate of the nuclear spins of the molecules:

$$1/\tau_{ce}=\langle v\sigma\rangle_{ce}[\mathrm{Cs}]. \tag{10}$$

Here $\langle v\sigma\rangle_{ce}$ is the rate constant.[11]

The accuracy of our data is too poor to allow us to make a very accurate determination of the relaxation rates due to chemical exchange and the molecular hfs. However, from the data of Fig. 2 it is clear that something in addition to molecular breakup is limiting the relaxation time, since the relaxation time at lower pressures is too short to be explained solely by (5). A fairly good fit to the data of Fig. 2 can be obtained by choosing the rate constant for chemical exchange to be of the order of

$$\langle v\sigma\rangle_{ce} \simeq 10^{-10}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}. \tag{11}$$

The quadrupolar relaxation rate is then

$$1/\tau_Q \approx 7\times 10^{20}[\mathrm{Ne}]^{-1}\ \mathrm{cm}^{-3}\ \mathrm{sec}^{-1}, \tag{12}$$

which, together with (7), (8), and the measured value[7] of eqQ/h, yields a rate constant for relaxation of the rotational angular momentum of the molecules,

$$\langle v\sigma\rangle_J \simeq 3\times 10^{-11}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}. \tag{13}$$

We note that the rate constant for the randomization of J corresponds to a mean cross section of the order 10^{-15} cm^2, while the cross section for relaxation due to chemical exchange would be of the order 10^{-14} cm^2. Although the numbers (11), (12), and (13) are physically reasonable, they can only be considered as order-of-magnitude estimates at this time because our data have been taken over such a limited range of temperature and pressure, and the accuracy of the data is so poor.

The mechanism for detection of the NMR signals in our work is very similar to that of Dehmelt's[12] original spin-exchange work, and we shall limit ourselves to a qualitative description of the process. The reactions (4) and (9) can be expected to conserve both the electronic and nuclear spins of the cesium atoms and molecules. If these reactions proceed at a sufficiently rapid rate, the spin angular momentum of the molecules will be tightly coupled to the spin angular momentum of the atoms, and saturation of the nuclear spin polarization of the molecules with an rf field will also diminish the atomic spin polarization, which is monitored by the transmitted pumping light.

We have also observed good NMR signals for Cs^{133} in helium and argon buffer gases, and some measured relaxation rates for Cs in a 335-Torr helium buffer gas are shown in Fig. 2. The rates for breakup reactions like (4) do not appear to be very sensitive to the nature of the inert gas. Although good but broad NMR signals can be seen from $^{85}\mathrm{Rb}_2$ at neon buffer-gas pressures of 1250 Torr, the signal amplitudes are much smaller than those of $^{133}\mathrm{Cs}_2$ at lower pressures (150, 300 Torr). We believe that this is at least partially because of the faster quadrupolar relaxation of $^{85}\mathrm{Rb}_2$.

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