

## Measurement of the Rb- $^{131}\text{Xe}$ Spin-Exchange Cross Section in $^{131}\text{Xe}$ Relaxation Studies

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Estimates of the Rb- $^{131}\text{Xe}$  spin-exchange cross section have been obtained by observing the nuclear spin relaxation of  $^{131}\text{Xe}$  in the presence of a Rb vapor. Nuclear spin relaxation of  $^{131}\text{Xe}$  due to the presence of a foreign buffer gas and the relaxation rate on the glass walls of the cell have also been observed.

The spin-exchange process between the polarized valence electron of an alkali atom and the unpolarized nucleus of a noble-gas atom<sup>1</sup> has been of interest in the past both as a mechanism for polarizing noble-gas nuclei<sup>2-5</sup> and also as a source of relaxation for optically oriented alkali vapors.<sup>6</sup> We have recently measured the transverse nuclear spin relaxation of a gaseous  $^{131}\text{Xe}$  ensemble which had been polarized in collisions with an optically oriented Rb vapor. These measurements allowed for the first time the experimental determination of the spin-exchange cross section between the Rb valence electron and the nucleus of  $^{131}\text{Xe}$ . In addition, we have, to our knowledge, the first measurements of the nuclear spin-relaxation rates of  $^{131}\text{Xe}$  both on the glass walls of the experimental cell and in collisions with a foreign buffer gas in a low magnetic field. Similar measurements have been previously made for  $^3\text{He}$  in the presence of Rb (Refs. 2-4) and Na (Ref. 6) and for  $^{129}\text{Xe}$  in the presence of Rb.<sup>5</sup>

Previous measurements of the nuclear spin relaxation of  $^{131}\text{Xe}$ , which were done in pure xenon at high pressures, showed a relaxation time that was inversely proportional to the density of the gas.<sup>7</sup> The observed relaxation was attributed to a nuclear quadrupole interaction which is present during the collision of the xenon atoms. A theoretical study of this problem by Adrian<sup>8</sup> confirmed that the quadrupole interaction was the dominant relaxation mechanism of  $^{131}\text{Xe}$  in these samples. However, an extrapolation of Adrian's results to our sample densities<sup>9</sup> led us to expect relaxation times due to xenon-buffer-gas collisions of almost an order of magnitude longer than what we actually observed. The polarization of  $^{131}\text{Xe}$  through exchange with Rb then proved to be a more difficult problem than that associated with the other noble-gas nuclei.

Our experimental setup consists of a 15-ml

Pyrex sphere into which we distill an excess of Rb metal, and then fill with 0.5-Torr enriched  $^{131}\text{Xe}$  plus a buffer gas. The Xe gas is such that  $^{131}\text{Xe}$  constitutes 63.89 mole%,  $^{129}\text{Xe}$  is 0.7 mole%,  $^{83}\text{Kr}$  is 0.38 mole%, and the remaining is composed of even isotopes of Xe. The buffer gases used in this particular set of measurements were  $\text{H}_2$ ,  $\text{N}_2$ , and  $^4\text{He}$ . The cell is contained in a resistance-heated oven capable of controlling temperatures to  $\pm 0.1^\circ\text{C}$  up to  $120^\circ\text{C}$ . A three-axis set of Helmholtz coils surrounds the oven with the whole assembly contained in four cylindrically concentric magnetic shields, which reduce external magnetic fields to below  $10\ \mu\text{G}$ .

The experiment proceeds in two steps. In the first step, the Rb vapor is optically pumped in the longitudinal direction with  $\sigma^+D_1$  light provided by a dye laser. In this mode only a single magnetic field along the light beam direction is present in order to provide a quantization axis for the Rb electronic spin and the Xe nuclear spin.

The dye laser is a Spectra Physics model 375 with Oxazine-750 dye pumped by a Spectra Physics model-171 krypton-ion laser. The dye laser is employed because of the low polarization levels generated by pumping with the resonance lamp. The resonance lamp, although sufficient for similar measurements<sup>5</sup> in  $^{129}\text{Xe}$ , could not provide  $^{131}\text{Xe}$  signal at the high-temperature end. During the experiment, measurements of the laser power in front of the circular polarizer indicated power between 80 and 150 mW. There was no concern to keep the laser power stable as long as it remained above 80 mW. The laser wavelength was centered at  $7947.6\ \text{\AA}$  with a full width at half maximum of about  $1\ \text{\AA}$ .

The system was pumped for a time long enough to build up a significant Xe nuclear polarization. Neglecting the nuclear spin of the alkali, the noble-gas polarization can be expressed in terms

of the equilibrium Rb polarization as<sup>4</sup>

$$P_{Xe} = T_p P_{Rb} / T_{ex}, \quad (1)$$

where  $T_{ex} = (N_{Rb} \sigma_{ex} \bar{V})^{-1}$ , with  $N_{Rb}$  being the Rb number density,  $\sigma_{ex}$  being the Xe-Rb spin-exchange cross section, and  $\bar{V}$  being the Xe-Rb relative velocity.  $T_p$  is the time characteristic of the growth of the Xe nuclear polarization, which is given by

$$T_p^{-1} = T_{ex}^{-1} + T_1^{-1} \quad (2)$$

with  $T_1$  being the longitudinal nuclear-relaxation time. Pump times for the Xe in this experiment were on the order of minutes.

The second step in the experiment is to mechanize the Rb vapor as a magnetometer to detect the Xe magnetization as it precesses about a transverse axis. This is accomplished by switching off the longitudinal-axis pump field and switching on an 8-kHz drive field along an axis mutually perpendicular to the light beam direction and the transverse axis and a 100- $\mu$ G precessional field. In this detection mode, the resonance lamp and  $D_1$  filter are moved on axis to be used as the source of the detection beam, since it is a very low noise source of  $D_1$  light. The magnetometer mechanization, which was developed by Cohen-Tannoudji *et al.*,<sup>10</sup> has been previously discussed in terms of measuring noble-gas nuclear-spin-decay rates.<sup>5</sup> It can be shown that in this mode the transmitted light beam is modulated at the drive frequency and at the noble-gas nuclear-precession frequency with a modulation amplitude proportional to the Xe magnetization.

The decay of the Xe magnetization is characterized by a time constant,  $T_2$ , which we assume can be written in the following form:

$$T_2^{-1} = N_{Rb} \sigma_{ex} \bar{V} + \Gamma e^{2E/kT} + (T_2')^{-1}, \quad (3)$$

where the first term on the right-hand side of Eq. (3) represents the spin-exchange rate with the Rb vapor, the second term is a wall relaxation rate<sup>4</sup> (with  $\Gamma$  being the effective collision rate,  $E$  being the adhesion energy of the Xe atoms on the glass wall,  $k$  being Boltzmann's constant, and  $T$  being cell temperature in degrees kelvin), and the third term represents all other relaxation rates, which we assume are at most weakly temperature dependent.

The results of our measurements of the <sup>131</sup>Xe nuclear-spin-decay rate as a function of cell temperature are shown in Figs. 1(a) through 1(d), where the solid line in each plot represents a least-squares fit of the data with the functional

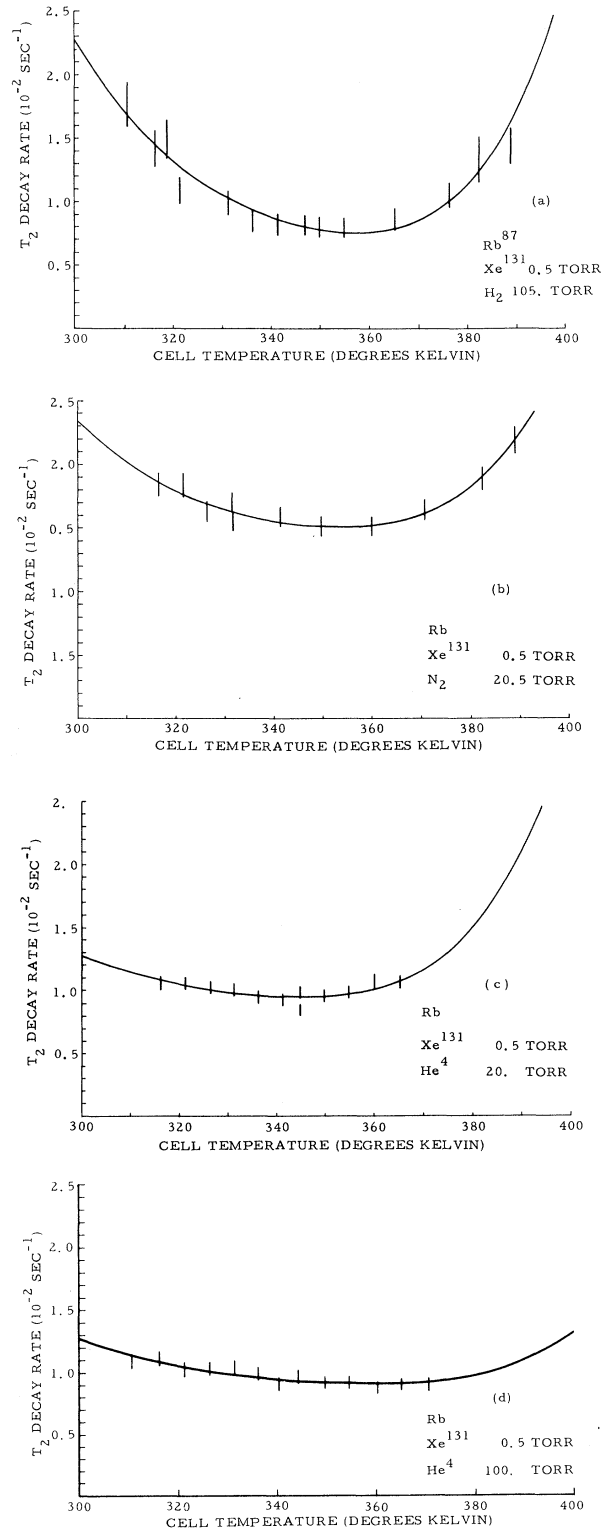


FIG. 1. <sup>131</sup>Xe relaxation rate vs cell temperature in the presence of (a) <sup>87</sup>Rb and 105-Torr H<sub>2</sub>, (b) natural Rb and 20.5-Torr N<sub>2</sub>, (c) natural Rb and 20-Torr <sup>4</sup>He, and (d) natural Rb and 100-Torr <sup>4</sup>He.

TABLE I. Least-squares-fit estimates of the  $^{131}\text{Xe}$  relaxation parameters in differently buffered cells. The 105-Torr  $\text{H}_2$  cell contained  $^{87}\text{Rb}$ , and the other three cells had natural Rb. All cells contained 0.5-Torr-enriched  $^{131}\text{Xe}$ .

Buffer gas (Torr)	$\sigma_{\text{ex}} \bar{V}^2$ [ $10^{-11}(\text{cm}^4 \text{sec}^{-2})$ ]	$\Gamma$ ( $10^{-8} \text{sec}^{-1}$ )	$E$ (eV)	$1/T_2'$ ( $10^{-3} \text{sec}^{-1}$ )
105 $\text{H}_2$	$5.96 \pm 0.4$	$3.89 \pm 0.2$	$0.13 \pm 0.01$	$1.54 \pm 0.5$
20.5 $\text{N}_2$	$4.27 \pm 0.1$	$0.40 \pm 0.02$	$0.16 \pm 0.01$	$12.5 \pm 0.5$
20 He	$6.06 \pm 1$	$1.47 \pm 0.5$	$0.13 \pm 0.01$	$7.42 \pm 1$
100 He	$1.3 \pm 2$	$2.85 \pm 0.5$	$0.12 \pm 0.01$	$7.47 \pm 1$

form of Eq. (3). Error bars represent a standard deviation based on reproduced measurements at selected temperature points. Evaluations of the relaxation parameters are given in Table I.

With reference to Table I, we make the following comments about our findings:

(1) Recently extensive measurements of the Rb- $^{129}\text{Xe}$  spin-exchange cross section, in the presence of  $\text{N}_2$  as a buffer gas, have been made.<sup>11</sup> As shown in Table I, the cross section for the Rb- $^{131}\text{Xe}$  exchange in the presence of 20.5-Torr  $\text{N}_2$  is a factor of 16 smaller than the cross section for Rb- $^{129}\text{Xe}$  in a similarly buffered cell. Using Herman's<sup>1</sup> expression for the spin-exchange cross section, one would expect cross section values for  $^{131}\text{Xe}$  to be about half those for the corresponding  $^{129}\text{Xe}$  cases. We think that this discrepancy may be due to an additional Rb-Xe interaction, if a quadrupolar type, which lessens the efficiency of the exchange process and hence lowers the measured cross section for  $^{131}\text{Xe}$ .

(2) The variation of the Rb- $^{131}\text{Xe}$  cross sections with buffer-gas pressure (see Table I) is expected in light of the influence of the Rb-Xe diatomic molecule on the spin-exchange interaction which has been established.<sup>11,12</sup> However, considering the comment in the previous paragraph, we do not expect the  $^{131}\text{Xe}$  cross section to have the same functional dependence on the buffer-gas pressure as was found for  $^{129}\text{Xe}$  (see Refs. 11 and 12).

(3) Since all the measurements were done in the same type cell, it is hard to say anything about the parameter  $\Gamma$  except that it is physically reasonable. The absorption energy,  $E$ , is of the right order of magnitude for the adhesion of Xe onto Pyrex.<sup>13</sup> A similar wall interaction has been observed in measurements of the relaxation of  $^{201}\text{Hg}$  in quartz cells.<sup>14-16</sup> The adhesion energy of Hg onto quartz derived from these measurements is found to vary by about a factor

of 2;  $E$  is given as 0.18 eV in Ref. 14 and as 0.34 eV in Ref. 16. The difference in these measurements was attributed to a dependence of the Hg relaxation on the cell-fabrication technique and cell-temperature history. We observed no dependence of the cell-temperature history on the relaxation of  $^{131}\text{Xe}$ . We are not sure whether this is due to the nature of the noble-gas relaxation or the nature of the cell material.

(4) The large difference between the constant rate,  $1/T_2'$ , measured in the  $\text{H}_2$  cell as compared to that found in the  $\text{N}_2$  cell, we attribute to a relaxation mechanism of the  $^{131}\text{Xe}$  in collisions with the buffer gas. This type of an effect has not been observed for  $^{129}\text{Xe}$  in similar cells, and thus we believe this interaction to be of a quadrupolar type. The lack of variation of the constant rate in the He-buffered cells may be due to the insensitivity of the He data to the least-squares fit.

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## Two-Photon Technique for the Dissociative Spectroscopy of Simple Molecules

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A two-photon technique is reported for the measurement of relative cross sections for the photolysis of simple molecules into particular product channels. In a demonstration of this method, two independently tunable dye lasers were used to dissociate molecules of Cs<sub>2</sub> sequentially for wavelengths in the range 445 to 505 nm, and then to excite the resulting products to determine the relative cross sections for the photolysis of the Cs<sub>2</sub> molecules into each of the energetically possible product states.

Historically, it has been the conventional techniques of absorption spectroscopy that have contributed most heavily to the understanding of the structure of simple molecules. However, the successes of these methods have been generally limited to the study of bound states. Comparable studies by conventional means of transitions to repulsive and dissociative states have usually led to featureless absorption continua and, thus, have not resulted in the depth of understanding that has been reached with the well-bound states of molecular systems.

The recent efforts which have developed in laser chemistry and laser isotope separation have tended to refocus spectroscopic interests upon these less tractable dissociative states. For example, if it is intended to activate selectively an isotopic or reactive species, photodissociation of a parent molecule appears, at first, to be a nearly ideal mechanism. Unfortunately, the practical application of such techniques generally requires detailed knowledge of the dissociative

state to be excited, of the states of the products with which it is correlated, and of the dynamics of the dissociation process which determine the extent to which the product channels might be mixed by crossings of the potentials describing long-range forces. The examination of spontaneous fluorescence from the products of laser-induced photolysis provides some of this information but it is generally susceptible to uncertainties in the unique identification of product channels unless the fluorescence lifetimes of the dissociation products are much less than the characteristic times for collisional mixing of the states, as was the case in the classical measurement<sup>1</sup> of the various partial cross sections for the photolysis of H<sub>2</sub>.

The work reported here concerns the demonstration of a sequential, two-photon technique for the study of laser photolysis. It is based on a multiphoton process originally observed in H<sub>2</sub> by LuVan *et al.*<sup>2</sup> and independently demonstrated by Collins *et al.*<sup>3</sup> In particular, it was found in