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Spin-Rotation Coupling in the Alkali-Rare-Gas Van der Waals Molecule KAr

Edward M. Mattison, David E. Pritchard, and Daniel Kleppner

*Research Laboratory of Electronics and Department of Physics, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139*

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We report results of a molecular-beam magnetic-resonance study of the paramagnetic Van der Waals molecule KAr. The experiment yields a value for the spin-rotation interaction $\hbar\gamma\vec{S}\cdot\vec{N}$, where $\hbar\vec{S}$ and $\hbar\vec{N}$ are, respectively, the electronic and rotational angular momentum. The average spin-rotation constant in KAr is $\bar{\gamma}=0.24(1)$ MHz.

We report here initial measurements of the magnetic-resonance spectrum of the Van der Waals molecule KAr. This type of molecule, which is bound only by the long-range dispersion force, has a binding energy on the order of 10^{-2} eV, less than 1% of a typical chemical bond. The attraction is great enough to form stable molecules from practically any two atomic or molecular species. Van der Waals molecules have been observed spectroscopically in a gas,¹ and several polyatomic systems have been studied by electric-resonance methods.² However, interactions in isolated diatomic molecules have not been observed previously.

Paramagnetic Van der Waals molecules are particularly appealing candidates for study by magnetic resonance³: Effects such as hyperfine coupling shifts and spin-rotation interactions, heretofore detected only in optical-pumping experiments, can be observed in detail. The present experiment is a study of the spin-rotation interaction $\hbar\gamma\vec{S}\cdot\vec{N}$ in KAr, where $\hbar\vec{S}$ and $\hbar\vec{N}$ are respectively the electronic and rotational angular momentum.

Bouchiat and co-workers⁴ found evidence for alkali-rare-gas molecules in optical-pumping relaxation studies of alkalis in a buffer gas. They showed that electron-spin relaxation in such systems can be explained by the spin-orbit interac-

tion in molecules that form in three-body collisions and dissociate at the next two-body collision. In the case of RbKr their results lead to an average coupling constant $\bar{\gamma}=0.63$ MHz, in rough agreement with an earlier calculation by Herman.⁵ γ varies with internuclear separation, so that its value depends on the rotational and vibrational state of the molecule. Since molecules in all internal states contribute to the relaxation in optical-pumping experiments, the technique is not well suited for obtaining details of the spin-rotation interaction. Attempts to observe magnetic resonance in the molecules via its effect on the relaxation rate have so far proven inconclusive.⁶

Our study of KAr employs a conventional molecular-beam magnetic-resonance apparatus designed to optimize the production and detection of paramagnetic Van der Waals molecules. The molecules are formed in a supersonic nozzle beam in which potassium ($p\sim 100$ Torr) and argon ($p\sim 2000$ Torr) emerge into a vacuum through an orifice 0.003 cm in diameter. A surface ionizer is used to detect the beam. Since the molecules dissociate prior to ionization, the detector cannot distinguish K atoms from KAr molecules. Consequently, special efforts are needed to separate the molecules from the much larger flux of atoms.

The principal discrimination mechanism is spatial separation by deflection in magnetic field gradients.⁷ A nozzle source produces a beam in which all species move with the same average speed. (The velocity distribution is similar to a narrow bell-shaped curve superimposed on a large translational velocity.) As a result, the deflections of K and KAr, which have identical magnetic moments, are inversely proportional to their masses. To enhance the spatial resolution, the "tails" of the narrow velocity distribution are removed by a slotted-disk velocity selector having a full width at half-maximum $\Delta v/v = 10\%$. Because of the relatively high beam velocity, approximately 10^5 cm/sec, and the need for large deflection, the deflecting magnets are unusually long for an atomic beam: length = 25 cm, gradient = 34 kG/cm. A detected beam flux of up to 4×10^4 KAr molecules per second has been obtained with a K impurity of less than 10%.

The trace of the resonance curve, Fig. 1, was obtained while operating the apparatus in the "flop-in" mode using a lock-in detector with a 5 sec time constant. The magnetic field in the resonance region was 19.5 G; the apparatus resonance width, limited by the molecules' transit time, was 22 kHz. The error bars represent the limits between which three curves, taken on different occasions, all lie.

The spectrum of Fig. 1 can be understood in terms of the Hamiltonian for the ground electronic state of KAr in an applied field \vec{H}_0 :

$$\mathcal{H} = ha\vec{I} \cdot \vec{S} + g_s \mu_0 \vec{S} \cdot \vec{H}_0 + h\gamma \vec{S} \cdot \vec{N},$$

where a is the hyperfine coupling constant, I and S are the respective nuclear and electronic spins, N is the rotational quantum number, and γ is the spin-rotation coupling constant. The experiment was carried out in a magnetic field such that $ha\vec{I} \cdot \vec{S} > g_s \mu_0 \vec{S} \cdot \vec{H}_0 > h\gamma \vec{S} \cdot \vec{N}$. In this regime \vec{I} and \vec{S} couple to form \vec{F} , and the energy of a single hyperfine multiplet is given to good approximation by

$$W(F, m_F, N, m_N) = g_F \mu_0 H_0 m_F + h\gamma g_F m_F m_N / 2, \quad (2)$$

where $g_F \cong \frac{1}{2}$. The first term on the right-hand side represents the coupling of the free atom with the magnetic field; the second term produces a fine structure due to the spin-rotation interaction.

We observed the Zeeman transition, $F=2$, $m_F = -1 \rightarrow m_F = -2$. The frequencies are given by

$$\nu = g_F \mu_0 H_0 / h + g_F \gamma m_N / 2. \quad (3)$$

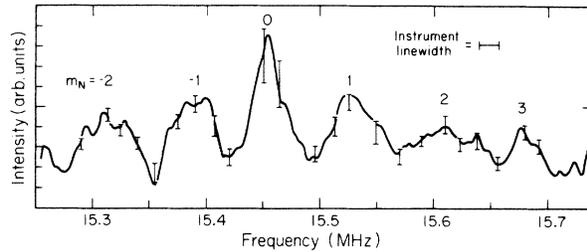


FIG. 1. Magnetic-resonance spectrum of KAr for the transition $F=2$, $m_F = -1 \rightarrow m_F = -2$, at a field of 19.5 G. The signs of m_N correspond to a positive value of γ . The error bars indicate limits within which three experimental spectra lie.

Thus for each value of m_N the Zeeman frequency is shifted by $g_F \gamma / 2$. The peaks in Fig. 1 are due to transitions with m_N ranging from -2 to $+3$. The average separation of these peaks is 72.9 kHz. For reasons described below, these peaks are not quite equally separated. The separations range from 67(1.5) to 78(2) kHz, with the separation increasing with $|m_N|$. The uncertainties represent statistical deviations in averaging three curves. From these values we have inferred a mean value of $\bar{\gamma} = 0.24(1)$ MHz.

The final uncertainty of our result reflects two aspects of the data which are under further investigation. One is the broadening and shifting of the resonance peaks caused by variations of γ with molecular vibration-rotation state; we hope to exploit this to determine the variation of γ with internuclear separation. The other is the shift of the center of the molecular resonance curve from the atomic Zeeman resonance frequency caused by a shift in the hyperfine atomic interaction in KAr relative to K. Both of these effects are complicated by off-diagonal elements of the spin-rotation interactions.

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Investigation of the Production of Noncharacteristic X Rays during Ar-Si Collisions at 270 keV

J. A. Cairns, A. D. Marwick, J. Macek,* and J. S. Briggs

Atomic Energy Research Establishment, Harwell, Didcot, Berkshire, United Kingdom

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This study elucidates the role played by implanted argon in the production of Ar *L*, non-characteristic, and Si *K* x rays during 270-keV argon bombardment of silicon carbide.

Recent observations¹⁻⁶ of noncharacteristic x rays produced during bombardment of solids by energetic heavy ions have been interpreted¹ as being due to inner-shell transitions during the lifetime of the pseudomolecule formed during an atomic collision. In this paper we present a study of the phenomenon, in which the relationship between characteristic and noncharacteristic x rays is clarified. The system studied is Ar + Si, since three groups of x rays arise, which can be easily resolved; namely Ar *L* (~220 eV), noncharacteristic (whose distribution appears to peak at 1 keV because of the strong attenuation exhibited by the detector window for the lower energy components), and Si *K* (~1800 eV).

The Fano-Lichten model⁷⁻⁹ of heavy-ion x-ray production predicts that no Si *K* x rays are produced in a single collision between argon and silicon atoms, because the 1s electrons of silicon would have to be promoted to the argon 2*p*, which is already full. The fact that Si *K* x rays are generated was explained by Macek, Cairns, and Briggs¹⁰ as arising from a double scattering in which an argon 2*p* vacancy created in a prior collision is carried into a subsequent Ar-Si collision, thereby permitting Si *K*-electron promotion. The production of noncharacteristic x rays is thought to be an alternative process during the same collision. It thus becomes apparent that all three x-ray yields, viz. Ar *L*, noncharacteristic, and Si *K*, are interrelated.

The x-ray yields measured in our experiment are shown in Fig. 1. Targets of silicon and sili-

con carbide were bombarded with 270-keV Ar⁺⁺ ions. The x rays emitted were detected with an end-window proportional counter¹¹ and single-channel-analyzers were used to obtain the yields of the three x rays. The yields are not corrected for absorption in the counter window. However, the rate of buildup of the x-ray yields shown in Fig. 1, expressed as a fraction of their initial yields extrapolated to zero dose, can be correctly determined from the data, as can differences in intensity between silicon and silicon-carbide targets.

In their original study of this system, Saris, van der Weg, and Tawara¹ observed that the non-

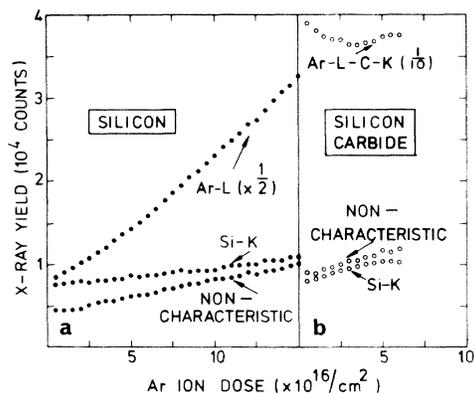


FIG. 1. The yields of Ar *L* (220 eV), noncharacteristic (band), and Si *K* (1739 eV) x rays under 270-keV Ar⁺⁺ bombardment as argon dose is increased. The yields of all three x rays are higher in the case of SiC targets.