MOLECULAR-BEAM RESONANCE MEASUREMENT OF DEUTERIUM POLARIZABILITY ANISOTROPY*

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(Received 20 February 1970)

The molecular-beam magnetic resonance method has been used to measure directly the anisotropy of the static electric polarizability of the deuterium molecule. This is the first measurement of this quantity for any molecule using the molecular-beam resonance method.

In this Letter we report on a direct determination of the anisotropy in the static electric polarizability of the deuterium molecule D_2 using the molecular-beam magnetic resonance method. This is the first measurement of this quantity for any molecule using a molecular-beam resonance method. The result for deuterium is of interest because there are very accurate theoretical calculations[1] of the anisotropy which may be compared with the experimental value.

The apparatus used for this experiment is the molecular-beam magnetic-resonance spectrometer described by Baker et al.[2] with a number of subsequent modifications, the most important of which are the improved electron-bombardment detector,[3] a liquid-nitrogen-cooled, supersonic nozzle beam source,[4] and a pair of electric field plates. The Stark effect of the nonpolar D_2 molecule[5] is observed as a shift in the frequency of the usual magnetic resonance transition (Zeeman or hyperfine) due to the presence of a large static electric field in the resonance region of the apparatus. This highly uniform electric field is produced by two flat, parallel plates[6] which are placed inside the radio-frequency coil which induces the transitions. This prevents any distortion of the homogeneous electric field by the conductor which forms the coil. At the transition frequencies (248 to 1840 kHz) encountered in this experiment, the presence of the plates inside the rf coil is not expected to alter significantly the oscillating fields which would exist in the apparatus if the plates were absent. The plate spacing is kept small (0.145 cm) because the rf coil with plates inserted must be sufficiently thin to fit within the 0.8-cm gap between the pole faces of the C magnet. The values of electric field used experimentally are determined by dividing the voltage between the plates (which is stable and measured to better than 0.1 %) by the thickness of the glass spacers[6] which separate the plates.

The Hamiltonian and energy levels of D_2 in the absence of any electric fields have been given previously by Ramsey.[7] If we denote his Hamiltonian by $\mathcal{H}_0$, then in the presence of a static, homogeneous electric field, the total Hamiltonian for the $J=1$ rotational state of D_2 may be written as

$$\mathcal{H}=\mathcal{H}_0-\tfrac{1}{3}\gamma E^2P_2(\cos\theta)-\tfrac{1}{2}\alpha E^2,$$

where $P_2(\cos\theta)=\frac{1}{2}(3\cos^2\theta-1)$ is a Legendre polynomial, θ is the angle between the internuclear axis of the molecule and the external electric field $\vec{E}$, $\gamma=(\alpha_{\parallel}-\alpha_{\perp})$ is the anisotropy, and $\alpha=\frac{1}{3}(\alpha_{\parallel}+2\alpha_{\perp})$ is one-third the trace of the polarizability tensor, and where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the molecular electric polarizabilities for electric fields parallel and perpendicular to the internuclear axis, respectively. This form of the Hamiltonian is valid when the electric field $\vec{E}$ is parallel to the static magnetic field $\vec{H}$ of the C magnet, which corresponds to the experimental conditions. The last term in the Hamiltonian has diagonal matrix elements only and therefore shifts all energy levels of interest by the same amount; in this experiment, it can be neglected completely. The effect of the second term on the energy levels depends on the size of the terms in the Hamiltonian which depend on H and E relative to those terms which describe the internal molecular interactions (e.g., quadrupole, spin-rotation, and spin-spin interactions). If the external magnetic field $\vec{H}$ is sufficiently strong, then the nuclear and rotational magnetic moments are effectively uncoupled and each precesses independently about the direction of the static field $\vec{H}$; this is the so-called strong-field approximation. In this case, the magnetic resonance transitions of interest here correspond to reorientations of either the nuclear or rotational magnetic moments relative to the direction of the static magnetic field. It is found that in an electric field $\vec{E}$, the frequencies of the transitions which reorient the molecule's angular momentum are shifted by an amount $\frac{1}{5}\gamma E^2$. The shift may be either up or down depending on the transition. The frequencies of transitions which reorient the nuclear spins, however, are unaffected in this approximation because there is no direct interaction[8] between the resultant nuclear spin $\vec{I}$ and the external electric field. For the values of static magnetic and electric field used experimentally, the strong-field approximation gives results accurate only to a few percent so that it is necessary in practice to diagonalize the Hamiltonian matrix directly using a simple computer program.

We have observed the Stark shift for the rotational reorientation transition EF [7,9] $(I,J,M_I,M_J=1,1,0,0) \leftrightarrow (I,J,M_I,M_{J'}=1,1,0,1)$, as a function of both H and E. 65 values of this shift, ranging from 29 to 235 kHz, have been observed for values of H from 1 to 4 kG and values of E from 17.9 to 49.9 kV/cm. From these data, a value of γ has been obtained using the least-squares method[10] and an iteration procedure which directly diagonalizes the Hamiltonian matrix for $I=J=1$. The result is that $\gamma = 0.2897$ Å^3. The statistical uncertainty[10] of ±0.10% (70% confidence interval) is negligible compared with the systematic uncertainty which arises from uncertainties in the spacing of the electric field plates. We estimate that because of these uncertainties our value of γ might be as much as 3% high or 1% low.

A check was made to see if the Stark shift for transition EF is dependent upon the direction of the electric field relative to the magnetic field,[11] by reversing the polarity of the voltage applied to the electric field plates. This was done for $H=1010$ G and $E=30.2$ kV/cm. The difference between the shifts for the two polarities is found to be (0.01 ± 0.20) kHz where the quoted statistical uncertainty represents one standard deviation.

Experimental checks for possible systematic errors have been made and calculations carried out to estimate the influence upon the Stark shift of phenomena such as motional electric fields, misalignment of the static $\vec{E}$ and $\vec{H}$ fields (assumed parallel when calculating γ from the data) resulting in a nonzero component of $\vec{E}$ perpendicular to $\vec{H}$, and the Bloch-Siegert effect.[12] These calculations and experimental checks indicate that for the conditions under which the data were taken, any errors introduced in this way are negligible. It is our intent to give a discussion of possible systematic errors and other details of this experiment in a future article.

A theoretical value of the polarizability anisotropy for the $v=0$, $J=1$ vibrational-rotational state of D_2 has been calculated by Kołos and Wolniewicz.[1] They obtain $\gamma = 0.2908$ Å^3 which differs from our result by 0.4%. As noted by Kołos and Wolniewicz,[1] the anisotropy of H_2 is of interest in connection with a proposal by Golden and Crawford[13] that the intensity of the $J=1 \rightarrow 3$ rotational Raman transition in H_2 be used as an intensity standard for the determination of absolute Raman intensities of other molecules in the gas phase. The use of H_2 in this way requires that the value of γ be accurately known. Although the present experiment yields a value of γ for D_2 rather than H_2, the good agreement with the theoretical value of Kołos and Wolniewicz gives added confidence in their theoretical value for H_2.[14]

To our knowledge there is no other experimental value of γ for D_2 with which to compare our result; however, there does exist a value of γ for H_2 which has been obtained by Nelissen, Reuss, and Dymanus[15] using a molecular-beam deflection method. In this experiment α is measured by observing the deflection of a velocity-selected molecular beam of H_2 in an inhomogeneous electric field, and the quantity $\kappa = \gamma/3\alpha$ is measured using the E-H gradient-balance method.[16] The results obtained are $\alpha = 0.82$ Å$^3 \pm 2.4\%$ and $\kappa = 0.112 \pm 1.8\%$ which may be combined[17] to give $\boldsymbol{\gamma} = \mathbf{0.275_5}$ **Å^3 ± 3%. This value of $\boldsymbol{\gamma}$ is 9%** less than the value calculated by Kołos and Wolniewicz[1] for H_2. A direct comparison between our result (for D_2) and that of Nelissen, Reuss, and Dymanus (for H_2) cannot be made; however, in view of the good agreement (0.4%) between our value and that of Kołos and Wolniewicz (for D_2), the value of γ for H_2 obtained by Nelissen, Reuss, and Dymanus appears to be lower than our value by about 9%.[14] This difference is significant compared with the sum of the quoted experimental uncertainties of 6%.

The measurements on D_2 are being continued with the goal of reducing the systematic uncertainty in γ, and it is planned to measure γ for H_2 as well. In addition to these measurements, there appears to be no reason why the method cannot be extended to include other homonuclear, diatomic molecules which have been studied previously using the molecular-beam magnetic-resonance method. D_2 and H_2 have the advantage that single transitions can be resolved whereas larger molecules such as N_2 and F_2 generally exhibit magnetic-resonance spectra which are a superposition of many transitions. On the other hand, these heavier molecules are expected to have significantly larger γ's so that their Stark shifts should be correspondingly greater and should therefore be observable even for unresolved, overlapping transitions. Measurements on these heavier molecules are of interest for purposes of comparison with theoretical values calculated using perturbed Hartree-Fock techniques.[18]

We would like to thank Professor Norman Ramsey for encouragement and support. We are grateful to Ed McGaffigan, Jr., and Lew Lipson for assistance in apparatus fabrication and in data taking.

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*Research supported jointly by the National Science Foundation and the Office of Naval Research.

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[1] W. Kołos and L. Wolniewicz, J. Chem. Phys. 46, 1426 (1967).

[2] M. R. Baker, H. M. Nelson, J. A. Leavitt, and N. F. Ramsey, Phys. Rev. 121, 807 (1961).

[3] I. Ozier, thesis, Harvard University, 1965 (unpublished).

[4] A. Khosla, (unpublished).

[5] Deuterium was studied rather than hydrogen because the signal-to-noise ratio for D_2 is significantly better than for H_2 in the apparatus used; this is due to the large background of singly ionized particles of mass 2 amu in the electron-bombardment detector.

[6] The plates and spacers were fabricated by the A. D. Jones Company of Burlington, Mass.

[7] N. F. Ramsey, Phys. Rev. 85, 60 (1952).

[8] The terms in the Hamiltonian which describe the interaction of the molecule with the external electric field are independent of nuclear spin. In this sense there is no "direct interaction" between $\vec{E}$ and the nuclear spin; however, there is a direct interaction between $\vec{E}$ and the molecular rotation, so that an indirect coupling between $\vec{E}$ and $\vec{I}$ exists at weak and intermediate magnetic fields due to the direct coupling between nuclear spin and rotational motion.

[9] The linewidth (full width at half-intensity) of this transition is on the order of 10 kHz and is in good agreement with the value calculated on the basis of the uncertainty principle.

[10] J. R. Wolberg, Prediction Analysis (Van Nostrand, Princeton, N. J., 1967).

[11] Should such a shift exist, it could be due to terms proportional to odd powers of E appearing in the molecular Hamiltonian, or to a systematic effect such as a motional H field.

[12] N. F. Ramsey, Molecular Beams (Oxford University, Oxford, England, 1956), p. 122.

[13] D. M. Golden and B. Crawford, Jr., J. Chem. Phys. 36, 1654 (1962).

[14] This statement is based on the belief that the calculations of Kołos and Wolniewicz should predict isotope shifts quite accurately; support for this belief is provided by the good agreement between the calculated values of the isotope shift in the quantity α and the corresponding experimental results (see Table V of Ref. 1).

[15] L. Nelissen, J. Reuss, and A. Dymanus, Physica 42, 619 (1969).

[16] B. Bederson and E. J. Robinson, in Advances in Chemical Physics, Molecular Beams, edited by J. Ross, (Interscience, New York, 1966), Vol. 10, Chap. 1.

[17] Since the two measurements are independent, the uncertainties have been combined in quadrature.

[18] W. N. Lipscomb, Advances in Magnetic Resonance (Academic, New York, 1966), Vol. 2, p. 137.

DELAYED NEUTRONS FROM NEUTRON-IRRADIATED LiF CONTAINING COLOR CENTERS*

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It is shown that the neutron-electron interaction is orders of magnitude too small to allow neutrons to be bound to electron-excess color centers in alkali-halide crystals, as was indicated experimentally by Grant and Cobble.

In a recent Letter,[1] Grant and Cobble presented evidence that LiF crystals containing electron-excess color centers had the ability at 4°K to retain reutrons for ~40 sec. They concluded that a neutron-electron bound state existed. In this Letter, we calculate the neutron-electron interaction and find that this interaction is orders of magnitude too weak to lead to binding.

We first obtain a lower limit on the hypothetical neutron-electron binding energy, based on Grant and Cobble's data. They expose their LiF crystal to 4.8×10^8 thermal neutrons, and find that ~2 appear later. If we assume that only neutrons whose kinetic energy is less than the binding energy will be trapped, neglect any other fates for the incident neutrons (e.g., $\mathrm{Li}^6+n\rightarrow\mathrm{Li}^7$), assume a Maxwellian distribution for the incident neutrons, and assume that all trapped neutrons are detected, we find that the binding energy must be at least 4.4×10^{-5} eV.

We also estimate, using the uncertainty principle, the kinetic energy of a neutron confined to one atomic volume (e.g., an F center). We obtain $\sim10^{-4}$ eV.