Appearance-potential measurements and the observation that the formation of CH_5^+ is greatly retarded by the presence of SiH_4 suggest that CH_4^+ is the ionic precursor to SiH_5^+. The reaction is of higher order than second, however, because, as seen in Fig. 1(b), the fraction of ionization due to m/e 37 increases with the square of the ion-source pressure and indicates that two neutral molecules are involved in the reaction. Thus we write for SiH_5^+ formation the reaction

$$CH_4^+ + SiH_4 + M \rightarrow SiH_5^+ + CH_3 + M, \qquad (2)$$
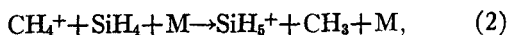
where M may be either CH_4 or SiH_4.

Since (2) is observable in a mass-spectrometer ion source at ion-source pressures of the order of 10^{-2} torr, we may conclude[7,8] that it is exothermic or thermoneutral. This assumption leads to the result that the proton affinity of SiH_4 must be at least 4.9 eV.

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Observation of Optical Radio-Frequency Double Resonance in Molecular Fluorescence*

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Microwave, ESR, and molecular beam resonance studies have produced a wealth of experimental data on the ground states of gas-phase molecules. Recently these radio-frequency techniques have been successfully extended to the study of some metastable states.[1] However, the study of short-lived excited states by these methods appears to be impractical due to the low concentrations of such species which can be achieved.

We describe here observations of a double resonance technique which we believe to be quite useful in, and generally applicable to, the investigation of short-lived molecular excited states. This is an indirect method whereby rf transitions in the excited state of a gas-phase molecule are detected by their effects on the optical photons emitted in fluorescence.[2,3] This optical radio-frequency double resonance (ORFDOR) technique is an extension to molecules of the Brossel–Bitter-type experiments on atoms.[4]
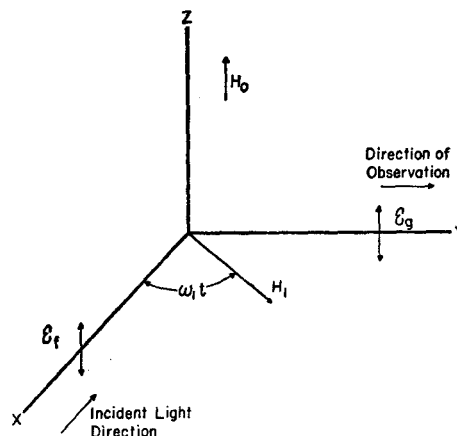

FIG. 1. Geometry of the experimental setup. Light from a lamp at X is incident upon a cell of nitric oxide (at about 0.1 torr pressure) located at the origin, and fluorescence is observed by a photomultiplier positioned at Y. Both polarization vectors $\mathcal{E}_f$, $\mathcal{E}_g$ and the static magnetic field H_0 are parallel to Z. A radiofrequency field H_1 oscillates with a frequency ω_1 parallel to Y, and may be resolved into two counter-rotating components in the XY plane

The experiments have been performed on the $v'=1$ level of the $A\,{}^2\Sigma^+$ state of nitric oxide. Light from either a cadmium or zinc lamp (which selectively excites the $K'=13$ or $K'=19$ rotational levels, respectively[5,6]) propagates along the X direction, polarized parallel to a magnetic field H_0 along the Z direction (see Fig. 1). Because of different angular-momentum coupling schemes in the ground and excited states, the incident polarized light coherently excites the magnetic sublevels of the excited state. The rf field H_1 rotates in the XY plane with a frequency ω_1. At resonance, H_1 mixes the magnetic sublevels of the excited state, inducing changes in the intensity of the resonance fluorescence[7] viewed along the Y direction polarized parallel to Z.

Two experimental runs are shown in Fig. 2. In trace (a) the output of a photomultiplier located along the Y axis is plotted versus magnetic field H_0. The use of an audio-frequency field to modulate H_0 in conjunction with a phase-sensitive detector produces the derivative signal shown in (b). We find that the behavior of ω_1 versus H_0 is linear over the range of 1–4 G, with the same slope for both rotational levels.[8] The data for the $K'=19$ level can be expressed to within 2% by $\omega_1 = 0.582 + 1.998H_0$, where ω_1 is in megahertz and H_0 in gauss. This slope corresponds to 1.43 β_0/G. The nonzero intercept represents a small but real splitting of the excited-state magnetic sublevels in the absence of an external magnetic field and might be accounted for by spin–rotation interaction.[9]

In conjunction with earlier experiments on zero-field level crossings in these states[6,10] in which we measured $\Delta E\tau/\hbar$ as a function of magnetic field (where ΔE is the energy separation of the sublevels responsible for the level crossing[11] and τ is the radiative lifetime), we find $\tau = (2.09 \pm 0.16) \times 10^{-7}$ sec for the $v'=1$ level. This
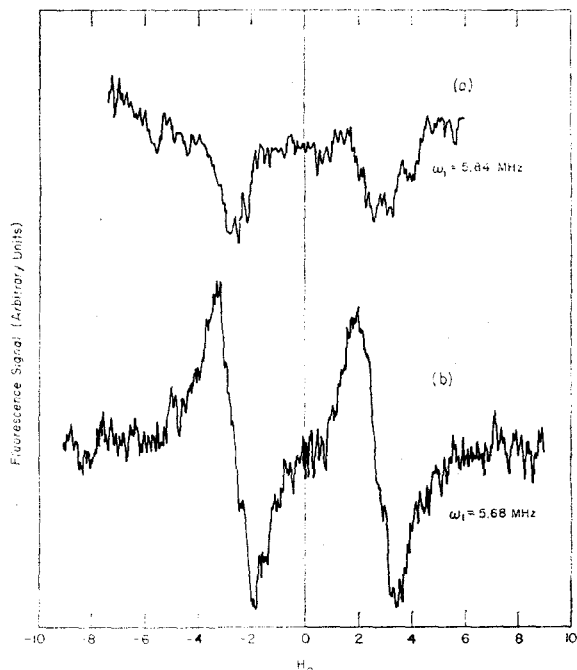
FIG. 2. ORFDOR signal tracings: (a) the dc response of the photomultiplier (b) the derivative signal obtained by the lock-in amplifier. The static magnetic field H_0 is measured in gauss.

agrees well with the band lifetime, $\tau = (1.965 \pm 0.03) \times 10^{-7}$ sec, determined by Jeunehomme[12] using electron-impact excitation. Thus ORFDOR experiments, by measuring ΔE as a function of external field, provide information on the detailed structure of molecular excited states—and, together with molecular level-crossing studies, furnish independent values of the radiative lifetime and permit, as well, the investigation of the collisional destruction of the coherence.

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Molecular Motion in Substituted Acetylenes in the Liquid State*

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NMR studies of spin–lattice relaxation times, T_1, in liquids provide detailed information about molecular motions in the liquid state (see, e.g. Ref. 1). For nuclei with spin $I > \frac{1}{2}$ the quadrupole interactions are usually the dominant relaxation mechanism; for spin $I = 1$ the relaxation rate $1/T_1$ is given by the following expression[2]

$$1/T_1 = \tfrac{3}{8}(1 + \tfrac{1}{3}\chi^2)(e^2 qQ/\hbar)^2 \tau_c, \tag{1}$$

where χ is the asymmetry parameter, $(e^2 qQ/\hbar)$ is 2π times the quadrupole coupling constant in hertz, and τ_c is the reorientational correlation time. For the systems investigated in the present study, τ_c is the rotational correlation time. If the quadrupole coupling constant is known, then one can calculate τ_c from measured T_1 as it was originally proposed by Moniz and Gutowsky.[3] Weiss and Flygare[4] have recently found that the deuteron field gradients are relatively insensitive to the nature of the substituent R in the R–C≡C–D compounds. Therefore, the –C≡C–D grouping can be used as a probe to study rotational motion in molecular liquids of the R–C≡C–D type. Using this procedure one has to assume that $(e^2 qQ/h)$ obtained in the gaseous state is applicable for the liquid[5] and that there is no association in the liquid.

The purpose of this investigation was to obtain the rotational correlation times, τ_c, for phenylacetylene-d_1 and methylacetylene-d_1 in the liquid state by measuring the deuteron T_1. The experimental rotational times obtained from Eq. (1) were compared with those calculated from the viscosity of the solution using Stokes[6] (S), Gierer-Wirtz[7] (GW), and Hill[8] (H) models, thus, providing a test of the individual models. In phenylacetylene in which the dipolar interactions are the single operative relaxation mechanism (at low temperatures) the intramolecular and intermolecular (see, e.g., Refs. 9, 10) contribution to relaxation was separated by measuring T_1 both of ring protons and