zinc compound as assigned by Bürger, Sawodny, and Wannagat.[6] The spectra are very similar except for the metal–nitrogen asymmetric stretching vibrations (Co, 362 cm^{-1}; Zn, 436 cm^{-1}). The much lower force constant suggesting weaker M–N bonds is consistent with the apparent lower thermal stability of the cobalt compound compared with the zinc compound.

The magnetic susceptibility was determined by the Gouy method over the temperature range 300–80°K and the Curie plot gave a magnetic moment of 4.83 BM independent of temperature. The orbitally nondegenerate ground state ($^4\Sigma_g^-$) would be consistent with this result (μ_{eff} independent of temperature). The large deviation from the spin only value indicates that either there is a very large TIP contribution or large spin–orbit coupling. The latter would seem most probable as the ligand field splitting by two nitrogens would not be expected to be large, thus allowing the "mixing-in" of nondegenerate excited states.

The cobalt silylamide is the only thermally stable dialkylamide of cobalt(II) so far prepared. Attempts to prepare $Co[N(C_2H_5)_2]_2$ gave a low yield of bis(N,N-diethylbutane-2,4-diiminato)cobalt(II).[7] Larger alkyl groups such as isopropyl gave green hexane-soluble compounds which were thermally unstable and difficult to purify, but which reacted with alcohols to yield alkoxides.

The cobalt silylamide reacted with alcohols forming alkoxides which are under investigation as they appear to exhibit unusual properties. Carbon disulfide reacts with metal dialkylamides to form *N,N*-dialkyldithiocarbamates but it does not appear to give a straightforward reaction with the cobalt silylamide. With oxygen the cobalt complex forms a black polymeric liquid, but with nitric oxide it reacts to form a nitrosyl complex similar to the chromium dialkylamides.[8]

We conclude from the above evidence that $Co[N(SiMe_3)_2]_2$ is a monomeric two-coordinate compound of cobalt, but a single-crystal X-ray structure is planned to determine the structural details. The coordinatively unsaturated nature of this cobalt complex suggests reactivity with a variety of small donor molecules and also makes this compound useful for preparing other cobalt compounds not easily prepared by other methods (*e.g.*, the alkoxides).

Acknowledgment. One of us (K. J. F.) thanks Queen Mary College for a research studentship.

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Tunable Ultraviolet Laser Excitation of Formaldehyde. An Application of Nonlinear Optics in Chemistry

Sir:

Monochromatic excitation of molecules has long been a powerful tool in the study of chemistry. However, past methods have been based either on selected atomic lines, thus sacrificing tunability, or on separating out portions of a spectrally broad light source, thus sacrificing spectral bandwidth. The first lasers offer high peak powers as well as great spectral radiance, but are still limited to fixed wavelengths. With the recent advances in tunable lasers and in nonlinear optics, we have been able to develop a continuously tunable uv source with power output in the 100–200-kW range for pulses of 7-nsec (FWHM) duration and a spectral bandwidth of 1 Å (FWHM). With this light source, we have excited gaseous dideuterioformaldehyde (D_2CO) and have been able to obtain, through fluorescence decay, the lifetimes of known vibrational levels of the first singlet excited state.

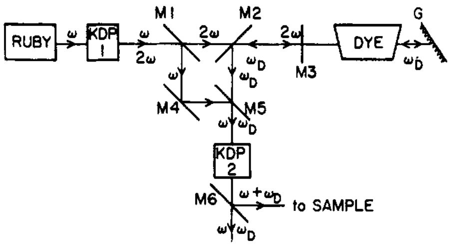

Figure 1. Apparatus for producing tunable uv radiation: (M1) 99% R at 6943 Å, 90% T at 3471 Å; (M2) 90% R at 5200–6500 Å, 85% T at 3471 Å; (M3) 16% R at 5200–6500 Å, 85% T at 3471 Å; (M4) 99.9% R at 6943 Å; (M5) 99% R at 6943 Å, 90% T at ≤ 6000 Å; (M6) 95% R at 3000–3500 Å, 95% T at 5000–7000 Å.

Our tunable uv source is based on obtaining a summation frequency by mixing in a nonlinear crystal[1] the 6943-Å output of a ruby laser and the continuously tunable output of an organic dye laser.[2] The optical arrangement used is shown in Figure 1.

A Pockels cell Q-switched giant-pulse ruby laser[3] produces 90 MW of 6943-Å radiation 25 nsec in duration. The ruby fundamental (ω) passes through a 1-in. long KDP (potassium dihydrogen phosphate) crystal cut 50° 35′ from the *c* axis (KDP1) and generates phase-matched[1] second harmonic radiation (2ω) at 3471 Å with 6-MW power and 15-nsec duration as measured with a TRG 108 thermopile. The second harmonic light is separated from the ruby fundamental by M1 and proceeds *via* M2 and M3 into the dye cell to pump the dye laser. The dye-laser cavity consists of an output mirror M3 with a 16% broad-band reflectance, a Bausch and Lomb grating blazed at 5000 Å (Littrow operation) with 1800 grooves/mm, and a 1-in. diameter, 0.75-in. long cylindrical dye cell with AR-coated $^1/_{16}$-in. thick quartz windows. We find that to ensure high output powers and narrow spectral spreads from the dye laser, the outer cylindrical wall of the cell must be frosted by grinding with carborundum, and the end windows must be tilted 5° off parallel, so that neither is parallel to M3. The summing process is polarization sensitive; the grating is placed with the grooves perpendicular to the direction of polarization of the ruby fundamental.[4] For some dyes, it is neces-

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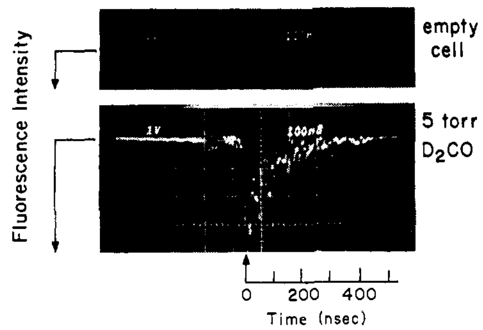

Figure 2. Fluorescence decay of D_2CO excited at 3139 Å.

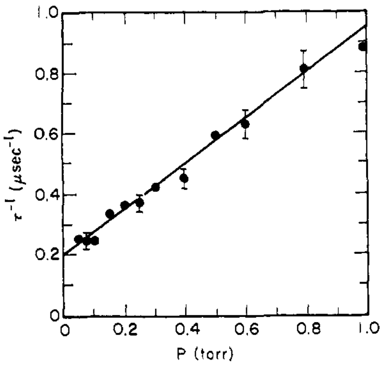

Figure 3. Stern–Volmer plot of inverse lifetimes of D_2CO excited at 3471 Å.

sary to further put a polarizing element in the dye cavity to obtain properly polarized laser output.

The dye laser output (ω_D) is 1 Å wide and can be tuned by suitable choice of dye, dye concentration, and grating position. Typically, for a 10^{-4} *M* solution of Rhodamine-6G in ethanol, the output at 5730 Å is 800 kW and 10 nsec wide, as measured on an Eppley bismuth–silver 16-junction thermopile. The dye laser is reflected by M2 through M5 onto the summing crystal. Meanwhile, the ruby fundamental is reflected by M4 and made collinear with the dye laser by M5. Summing is achieved by a 2-in. long KDP crystal (KDP2) rotated to the phase-matching angle of 56° 26′ for summing 6943 and 5730 Å to give 3139 Å. A tunable uv output of 200 kW has been measured by comparison with an attenuated beam of 3471 Å on a photomultiplier tube.

The uv radiation is separated from the visible radiation by M6 and passes into a 0.75-in. diameter Pyrex sample cell. Fluorescence is observed through a Spex 1400 double monochromator with slits parallel to the cell and detected by an Amperex 56AVP photomultiplier on a Tektronix 7704 oscilloscope. A typical trace is shown in Figure 2. It should be noted that one photon has a height of one-tenth of a vertical division. The trace shows the intrinsic photon counting fluctuation.

We have excited D_2CO with 3139-Å light, corresponding to 3 quanta of C=O stretching excitation[5] (3544 cm^{-1}). A lifetime for 4220-Å fluorescence emission (20-Å band width) of 103 ± 15 nsec was found. No observable pressure dependence was found from 3 to 10 Torr, corresponding to 3–10 collisions per lifetime.

We have also excited the 1 − level of the inversion[5] (501 cm^{-1}) of D_2CO with 3471-Å radiation and obtained an extrapolated zero-pressure lifetime of 5.0 ± 0.6 μsec. The Stern–Volmer plot of inverse lifetimes for observation at 4220 Å is shown in Figure 3. The plot is linear over the range of 0.05–10 Torr. The slope is 0.74 μsec^{-1} Torr^{-1}, corresponding to a quenching cross section of 1.2 Å^2.

With this experimental technique we hope to be able to study predissociation or intersystem crossing as a function of vibrational excitation of each normal mode. Experiments are under way with formaldehyde and its mono- and dideuterated species. The tuned-laser excitation method can easily be extended to study other molecules as well.

Acknowledgment. We wish to thank the National Science Foundation for a grant which supported this work.

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An Alternative to Donor–Acceptor Pseudocontact-Shift Nuclear Magnetic Resonance Shift Reagents[1]

Sir:

Recently a group of nmr shift reagents based on donor–acceptor bonds and the pseudocontact-shift effect have received much favorable and deserved attention.[2–8] The success of this group of shift reagents leads to an interest in other groups of reagents which can serve in complementary roles. This report describes one such group.

The reagents of this group rely on the ring-current effect of certain germanium–porphyrin systems for field asymmetry and on covalent bonds between the germanium atom of the porphyrin and the compound of interest for holding the reagent in place. The covalent bonds are formed by the reaction of appropriate functional groups on the macrocyclic germanium atom (halo or hydroxy groups) with appropriate groups on the compounds. Serving among the latter are ordinary organometallic groups (*e.g.*, the groups of organolithium and Grignard compounds) and both weakly acidic hydroxyl groups and strongly acidic hydroxyl groups (*e.g.*, the groups of alcohols, phenols, and carboxylic acids).[9] The utility of the reagents with

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(1) Support for this work was provided by the National Science Foundation through Grant No. GP-8368 and through a Traineeship.

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