

In general the ϕ_i 's may or may not be the united-atom potentials. Their choice is dictated by the rapidity of convergence and the ease of the ensuing calculation. The most convenient choices are Coulomb and Hooke's law potentials; the corresponding Ψ^{00} 's are then, respectively, hydrogenic and Hermite functions.

In the expansion in terms of Ψ^{00} 's, there exist in the secular determinant only three types of integrals: kinetic energy, nuclear attraction, and one-center electron repulsion integrals. Their evaluation (at least for hydrogenic or Hermite functions) is relatively uncomplicated. Problems of polycentric integrals naturally do not arise.

The alternate expansion, in terms of Ψ^0 , is superior in several respects. For well-chosen Coulomb potentials the E^0 's are just atomic (or ionic) term values where the electron repulsions are already minimized. Excellent tables⁴ are available, enabling detailed calculations in restricted cases, including that in which the ϕ_i 's are the true united-atom potentials. This semiempirical method is expected to converge faster than the corresponding *ab initio* calculation with the same ϕ_i 's.⁵ The true Ψ^0 's are, of course, unknown, but adequate approximations can be had in terms of, for example, Hartree-Fock, Morse-Young-Haurwitz⁶ and even nodeless Slater orbitals. Only one type of integral, the nuclear attraction integrals, needs to be evaluated here. An added feature is that, since the electron repulsion terms are already incorporated in H^0 , it is unnecessary to write antisymmetric determinantal wave functions, i.e., products of orbitals obeying naively the exclusion principle will do.

The choice of ϕ_i , however, is limited in the semiempirical method because of existent data. For instance, the best choice for H_2 is not the united-atom (He) potential, but that of the H^- ion; yet of the latter we have little knowledge beyond the ground state. The semiempirical method is most fruitful for problems of electronic spectra, where the absolute location of the ground state is unimportant. Otherwise, a more extensive table of ionization potentials would be required than is available.

Nuclear attraction integrals up to $(a|3d\delta3d\delta)$ are being evaluated with Slater orbitals of nonidentical exponents for 31 nuclear separations to 8 digit accuracy. The results will soon be published with applications.⁷

The writer wishes to thank Professor Hertha Sponer for her interest and encouragement.

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¹ P. M. Morse and E. C. G. Stueckelberg, *Phys. Rev.* **33**, 932 (1929).

² F. A. Matsen, *J. Chem. Phys.* **21**, 928 (1953).

³ R. D. Brown and F. A. Matsen, *J. Chem. Phys.* **21**, 1298 (1953).

⁴ *Atomic Energy Levels* compiled by Mrs. C. Moore (National Bureau of Standards, Washington, D. C.), two volumes in print.

⁵ This is analogous to the method of "atoms in molecules" of W. Moffitt [*Proc. Roy. Soc. (London)* **A210**, 245 (1951)] but used in a different context.

⁶ Morse, Young, and Haurwitz, *Phys. Rev.* **48**, 948 (1935).

⁷ After the completion of the first draft of the present note, the writer learned that Dr. R. K. Nesbet has programmed the MIT Whirlwind computer to evaluate all free atom one-center integrals involving Slater orbitals, and Dr. L. C. Allen and Dr. R. K. Nesbet together have independently developed an *ab initio* one-center method which is, however, different in emphasis from ours. See Quarterly Progress Report, Solid-State and Molecular Theory Group, MIT, July 15, 1955, pp. 27-29. The writer is indebted to Dr. Robert K. Nesbet for advance information.

Concentration Dependence of Solvent Shift in the C-H (and C-D) Stretching Frequencies of Chloroform and Pentachloroethane

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STRONG interaction of chloroform (and chloroform-*d*) with oxygenated solvents, e.g., ether and acetone, and basic solvents, e.g., pyridine and triethylamine, are known^{1,2} to give rise to large changes in the intensity of the C-H (and C-D) stretching band in the infrared. In some cases a new band, attributed to the hydrogen-bonded species, appears at a slightly lower frequency with an increased half-width and intensity.

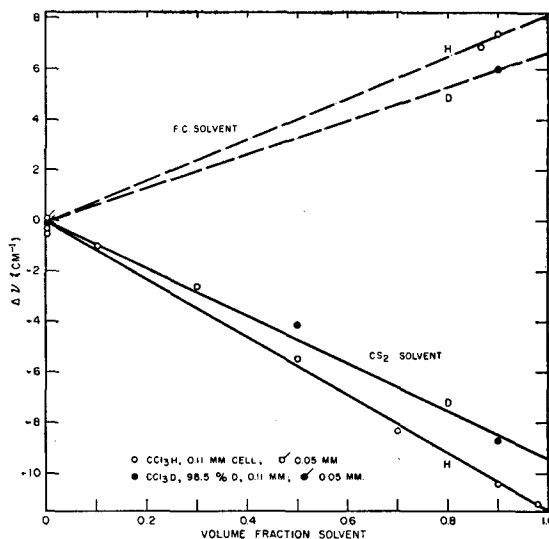


FIG. 1.

Small negative shifts in the C-H frequency are commonly noted even with "inert" solvents such as CS_2 and CCl_4 [where $\Delta H(\text{soln})$ is small and positive]. Reported here is the dependence of the frequency shift upon concentration and type of solvent for CCl_3H , CCl_3D , C_2Cl_5H , and C_2Cl_5D .

Figure 1 shows the shift, $\Delta\nu$ (cm^{-1}), as a function of the volume fraction of solvent for solutions of chloroform and chloroform-*d* in carbon disulfide and in a fluorochemical (type 0-75 of Minnesota Mining and Manufacturing Company³). Figure 2 shows similar plots for pentachloroethane and pentachloroethane-*d* in the same solvents. The data were obtained using a Perkin-Elmer Model 21 Infrared Spectrophotometer with a CaF_2 prism. Positions of the absorption maxima were reproducible to ± 1 cm^{-1} in the 3000 cm^{-1} (C-H) region and somewhat better near 2250 cm^{-1} (C-D).

The shift in the C-H (and C-D) frequency in CS_2 appears to vary linearly with concentration. The low solubility of the compounds in the fluorochemical limited the range of concentration that could be investigated. Similar observations on these solute molecules and on trichloroethylene in CS_2 and in CCl_4 were made using a NaCl prism, but with lower precision. The shifts for trichloroethylene appear to be smaller than those for the other two

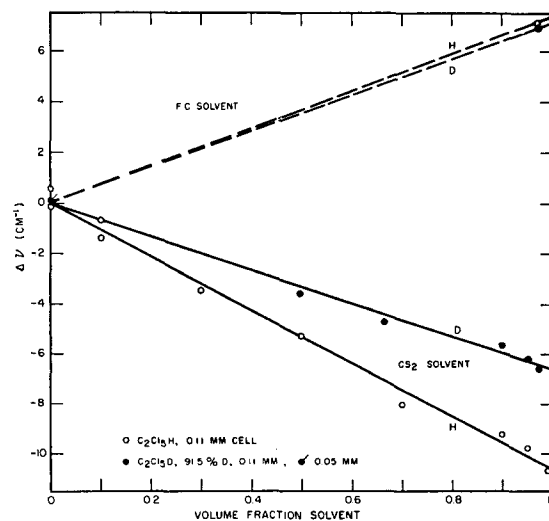


FIG. 2.

compounds, and the frequency shifts for all three compounds in CCl_4 are very slightly negative (ca 2 cm^{-1}).

The half-widths of the C-H band in CCl_3H and the C-D band in CCl_3D were $18 \pm 1\text{ cm}^{-1}$ and $10 \pm 1\text{ cm}^{-1}$, respectively (in agreement with reference 1), and showed no apparent variation with concentration of CS_2 . In the case of $\text{C}_2\text{Cl}_6\text{H}$ and $\text{C}_2\text{Cl}_6\text{D}$ the average values of the half-widths were 22 cm^{-1} and 12 cm^{-1} , respectively, although some variation with concentration was observed (decreased width with increased CS_2 concentration).

Further studies of spectral shifts, integrated intensities, and heats of mixing for these systems are in progress.

The authors acknowledge the assistance of J. C. Angus and T. J. Houser; the cooperation of Dr. G. B. M. Sutherland and Dr. D. L. Wood with regard to the use of the CaF_2 prism; and the financial support of the U. S. Atomic Energy Commission, and the H. H. Rackham Fund of the University of Michigan.

¹ Lord, Nolin, and Stidham, *J. Am. Chem. Soc.* **77**, 1365 (1955).

² C. M. Huggins and G. C. Pimentel, *J. Chem. Phys.* **23**, 896 (1955).

³ Stated to be a completely fluorinated cyclic ether with the empirical formula $\text{C}_8\text{F}_{16}\text{O}$.

Fluorescence and Average Lifetime of Excited $\text{OH}(^2\Sigma^+)$ in Flames*

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SPECTROSCOPIC studies show a nonequilibrium population of rotational levels of $^2\Sigma^+$ OH molecules in certain flames¹ and discharges.² Such results have been assumed to indicate a persistence of the initial rotational distribution produced in the process in which the electronically excited OH molecules are originally formed. It has been implicitly assumed that the OH remains in the excited state for the normal radiative lifetime of the electronic transition, $6 \times 10^{-7}\text{ sec}$,³ undergoing at atmospheric pressure about 1000 collisions before radiating. Persistence of rotation through so many collisions is surprising. If a radiationless transition, such as quenching by collisions, is important in removing excited OH molecules, the average lifetime of the state is decreased, and hence the molecules whose emission is observed will have undergone fewer collisions before radiating. This would make observed nonequilibrium distributions of rotational states less significant in implying long relaxation times, and more significant in terms of initial distributions. This letter reports measurement of fluorescence of OH in an atmospheric-pressure flame. Interpreting the result on the basis of quenching collisions indicates that the electronic energy of OH in the flame is removed by each collision.

The experimental arrangement is shown in Fig. 1. Most of the work was done in the outer cone of an oxy-acetylene flame burning on a commercial welding torch of port diameter 3.5 mm. Typical flow rates (cc/sec) were argon 15, oxygen 3.1, acetylene 1.5. In this flame, just above the inner cone, absorption of the strong $Q_1, 7$ and $Q_2, 2, 3$ lines of the 0,0 band is about 25%. An $f/10$ grating-monochromator with photoelectric detection⁴ was used with a slit width giving a resolution of 0.25 Å.

The measured fluorescence was about one part in 10^7 of the light incident on the flame. The fluorescence signal-to-noise ratio was 5. Scattering of light from the discharge into the monochromator and thermal emission from the flame were signals of the order of magnitude of the fluorescence. The possibility that the observed fluorescence is scattering from the flame was ruled out by the fact that no signal was found when the flame was illuminated with the 3131 Å doublet of mercury.

To calculate the importance of quenching, the ratio of the observed fluorescence, I , to that in the absence of quenching, I_0 , is needed,

$$I/I_0 = A/(A+Z),$$

where Z is the number of quenching collisions suffered per sec by

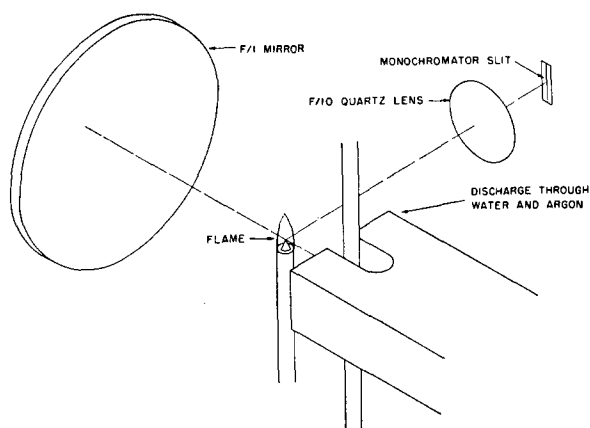


FIG. 1. Schematic diagram of apparatus. Various diaphragms and shields reduced scattered light.

one OH molecule, and A is the electronic transition probability for the free molecule. I_0 was estimated as the intensity absorbed by the flame, reduced by the factor $1/1600$ corresponding to the $f/10$ aperture of the monochromator. The intensity incident on the flame is taken to be the intensity observed in the monochromator when the discharge is in the flame position, times a factor of $100 [(F/1 : F/10)^2]$. In this way we measure $I/I_0 = 8 \times 10^{-4}$. Thus, the number of quenching collisions during the radiative lifetime of the free molecule is $Z/A = I_0/I = 1.3 \times 10^8$. At one atmosphere the number of collisions suffered by one molecule[†] is 1.6×10^9 per second, or 1×10^9 in the normal radiative lifetime. Hence $1.3/1.0$ of each kinetic theory collision leads to quenching, and the average lifetime of excited OH in the flame is of the order of 6×10^{-10} second.

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† Department of the Army, Aberdeen Proving Ground, Maryland.
¹ A. G. Gaydon and H. G. Wolfhard, *Proc. Roy. Soc. (London)* **A194**, 169 (1948); W. R. Kane and H. P. Broida, *J. Chem. Phys.* **21**, 347 (1953).

² O. Oldenberg, *Phys. Rev.* **46**, 210 (1934); H. P. Broida and W. R. Kane, *Phys. Rev.* **89**, 1053 (1953).

³ J. R. Dwyer and O. Oldenberg, *J. Chem. Phys.* **12**, 351 (1944); O. Oldenberg and F. F. Rieke, *J. Chem. Phys.* **7**, 485 (1939).

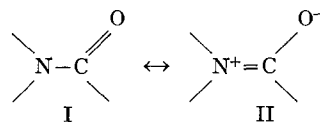
⁴ W. G. Fastie, *J. Opt. Soc. Am.* **42**, 641 (1952).

[†] By using a mean diameter of 2.7 Å, a reduced mass of 12, and $T = 2000^\circ\text{K}$.

Microwave Spectrum and Planarity of Formamide*

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THIS letter is a preliminary report of results from the microwave spectrum of formamide which show the molecule to be planar. This planarity is in accord with the resonance representation of the nitrogen-carbon-oxygen linkage in amides and polypeptides given by Pauling¹:



The sample used was vacuum distilled from Mathieson and Bell (99% pure) formamide; the fraction taken had a boiling point of 76.3°C at about two mm Hg pressure. The principal impurity removed by the distillation was methanol and the principal impurity remaining was ammonia (present only in small concentration, judging from the intensity of NH_3 lines observed). The spectrum was studied in the frequency range 14 kmc to 33 kmc, using a