### The 0–2 Transition of CO in Condensed Oxygen, Nitrogen, and Argon

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Infrared absorption spectra of CO in the region of the first overtone have been observed in dilute (approximately 1 to 10 parts in 1000) liquid solutions of oxygen, nitrogen, and argon, and clear crystalline nitrogen and argon matrices. The overtone band was found at 4249.0, 4252.4, and 4252.0 cm<sup>-1</sup> with half widths of 18.4, 17.8, and 13.7 cm<sup>-1</sup> in liquid oxygen, nitrogen, and argon solutions at 82, 78, and 82 °K, respectively. The half width in liquid oxygen varied from 18.4 to 10.0 cm<sup>-1</sup> in the temperature range 82 to 57 °K. The band position was the same but its width was smaller in the crystalline nitrogen matrix. Two bands were observed in the clear crystalline argon solid at 4245 and 4256 cm<sup>-1</sup>. The solution results cannot be interpreted with the recent theory of Buckingham.

Infrared absorption spectra of carbon monoxide in the region of the first overtone have been observed in the liquid solvents oxygen, nitrogen, and argon. In addition, the spectra have been obtained in clear crystalline solutions of argon and of nitrogen near the triple points of these solvents. The purpose of these experiments was to determine the influence of temperature, phase changes, and solvents on half width, position, and shape of the CO absorption band.

A Perkin-Elmer model 99 monochromator with a 2000 lines/cm grating blazed at  $10^{\circ}$  (1.7 $\mu$  in first order) was used in the first order with a spectral slit width of about 1 cm<sup>-1</sup>. An antireflection coated germanium filter eliminated the higher orders from the 1000 w tungsten filament lamp used as the light source. The quartz absorption cell used, recently described by Bass and Broida [1], was modified slightly by recessing the windows further into the coolant tube. The resultant increased thermal contact between the refrigerant and the solution greatly simplified the growing of the clear crystalline matrices. The temperature of the refrigerant, liquid oxygen, was regulated by pumping on it with a small vacuum pump (capacity 14 liters/min). The vapor pressure of the liquid oxygen refrigerant, measured with an aneroid type gauge, provided an indication of the temperature. The direct measurement of the vapor pressure above the solution with a mercury manometer also provided an indication of the temperature. Solutions were prepared from the gases which had been mixed in the ratios of 1 to 10 parts carbon monoxide to 1000 parts of the various solvents. The position, the half width, and the shape of the spectral band did not depend on the concentration in this range. The clear solid solutions were grown slowly from the liquids at or near the triple points of the solvents.

The measured frequencies and half widths of the 0-2 transition of CO in condensed oxygen, nitrogen, and argon are summarized in table 1. In liquid oxygen and liquid nitrogen, the band was symmetrical both at the half width and twice the half width and had a Lorentzian shape (using the width at twice the half-band width as the criterion [2]). There were no changes in the position or the shape of the band in liquid oxygen at temperatures from 57 to 82 °K. However the half-band width varied from 10.0 to 18.4 cm<sup>-1</sup> in this temperature range. In liquid argon the band is slightly asymmetric with more absorption on the high-frequency side.

Although the position of the band in clear crystalline solid nitrogen is not greatly different from that of the corresponding liquid solution, the half width is reduced by one-third and the shape is asymmetric and broader on the high-frequency side in the solid matrix. The absorption in the wings of the band is less than one would expect for a Lorentzian band shape. This observation is in apparent agreement with Wieder and Dows [3] who recently have observed vibrational bands of solid  $C_2H_4$  and  $C_2D_4$ which had shapes between the Gaussian and Lorentzian forms. In clear crystalline argon, the band is split into two overlapping peaks with the highfrequency peak about 50 percent more intense than the other peak.

Results for the band positions obtained in this study are in good agreement with the recently published results of Vu, Atwood, and Vodar [4]. The band contours which are shown by them appear quite similar to the ones observed in this study but half widths were not listed, so that a further comparison of our results with theirs is not possible. These workers did not study the influence of temperature on the spectrum.

In an effort to find an explanation for the observations of the 0–2 band of CO in condensed phases, several theoretical models have been tried.

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 $\begin{array}{cccc} {\rm Table \ 1.} & The \ {\rm O}{-2} \ transition \ of \ {\rm CO} \ in \ condensed \ oxygen, \\ nitrogen \ and \ argon \end{array}$ 

Solvent	Phase	Т	ν	$\Delta \nu_{\frac{1}{2}}$
020 02 Ar Ar N2 Ar	gas liq liq liq liq solid solid	${}^{\circ}K$ ${}^{300}$ ${}^{57}$ ${}^{82}$ ${}^{78}$ ${}^{82}$ ${}^{62}$ ${}^{67}$	$\begin{array}{c} cm^{-1} \\ 4260.\ 0 \\ 4249.\ 0 \ \pm 0.\ 5 \\ 4249.\ 0 \ \pm 0.\ 5 \\ 4252.\ 4 \ \pm 0.\ 5 \\ 4252.\ 0 \ \pm 0.\ 5 \$	$\begin{array}{c} cm^{-1} \\ 10.0 \pm 0.5 \\ 18.4 \pm 0.5 \\ 17.8 \pm 0.5 \\ 13.7 \pm 0.5 \\ 12.3 \pm 0.5 \\ 25.0 \pm 2.0 \end{array}$

Unfortunately none of these theories easily account for the band shapes and shifts.

Ewing [5] has observed the CO fundamental vibration in the liquid phase, in nitrogen and argon solutions. The bands he observed were not only asymmetric but also broader than the 0-2 bands observed in this study. The carbon monoxide fundamental had half widths of 26  $cm^{-1}$  and 18  $cm^{-1}$  in liquid nitrogen and argon, respectively, at temperatures comparable to those in this study. Ewing ascribed the asymmetry and increased absorption to the high-frequency side of the bands to a low barrier to rotation. From the asymmetry he estimated the barrier to be  $42 \text{ cm}^{-1}$  in pure liquid carbon monoxide, while slightly lower and slightly higher barriers were estimated for carbon monoxide solutions in liquid nitrogen and argon, respectively. A comparison with the present results (table 1) shows that the harmonic band is about two-thirds as broad as that of the fundamental. Moreover, the lack of asymmetry of the band in liquid nitrogen coupled with its narrowness in comparison to Ewing's observations of the fundamental seems to indicate that either hindered rotation is not the disordering mechanism contributing to the band width observed, or the barrier is several times higher than kT.

The observation of a variation of the half width of the CO harmonic in liquid oxygen from 10.0 to  $18.4 \text{ cm}^{-1}$  in the temperature range of 57 to 82 °K is surprising in the light of existing theories. If the band contour is determined principally by a strong collision process, in which the duration of the collision is small compared to the time between collisions, a Lorentzian band contour should be observed. The half width of such a band should be proportional to  $T^{1/2}$  [6, 7]. The observed dependence is clearly a function of a higher power of the temperature.

If hindered rotation is responsible for the band width, then an increase in half-band width and asymmetry to the high-frequency side of the band is to be expected with a rise in temperature if the barrier is comparable to kT. If the barrier is much higher than kT the band width is independent of temperature. Since the population of the J levels of a rotator is proportional to  $T^{1/2}$ , one would expect the width of the band to vary roughly as  $T^{1/2}$  if free or hindered rotation is causing the observed breadth. The observed dependence of approximately  $T^{3/2}$ coupled with the lack of asymmetry seems to rule out this explanation for CO in oxygen.

It has recently been suggested by Rakov in application to organic materials that the width of bands could be represented by an exponential of the form

$$\Delta \nu_{1/2} = A \exp\left(-E/RT\right) \tag{1}$$

where E is the potential barrier for reorientation of the molecules [8, 9]. Rakov has further indicated that if Brownian motion is responsible for the observed band widths this E should be equivalent to the energy of viscous flow,  $E_{\rm vis}$ , which is defined by Glasstone, Laidler, and Eyring [10] through the relationship

$$\eta = B \exp\left(E_{\text{vis}}/RT\right) \tag{2}$$

where  $\eta$  is the viscosity of the liquid medium. Using the data in table 1 for the band width of the CO harmonic in liquid oxygen at 57 °K and 82 °K, one may calculate the *E* appearing in eq (1). This value of *E* is about a factor of two smaller than the  $E_{\rm vis}$ calculated for liquid oxygen in this temperature range from the available data on the viscosity of liquid oxygen [11]. It appears therefore that this theory does not fit the phenomena observed in this study.

Recently Buckingham [12, 13, 14] presented a theory to account for solvent effects on vibrational transitions of diatomic molecules. One of the unique predictions of this theory is that the (s-1) overtone of a diatomic molecule should be s times as broad as the fundamental. The half widths observed in this study of the first overtone of carbon monoxide are decidedly *smaller* than the widths of the fundamental in these same solvent systems observed by Ewing [5]. This indicates the failure of Buckingham's theory in predicting band widths for the simple system carbon monoxide in nitrogen and argon solutions. The solvent shifts  $(\nu_{vap} - \nu_{sol'n})$  observed for the carbon monoxide harmonic in nitrogen is 7.6  $cm^{-1}$ , which is about 2.5 times the solvent shift of 3  $cm^{-1}$  for the fundamental observed by Ewing. Buckingham's theory as well as the earlier theory of Kirkwood, Bauer, and Magat [15, 16] predicts that the solvent shift of the harmonic should be twice that of the fundamental.

In conclusion, the first overtone of carbon monoxide has been observed in condensed phases of oxygen, nitrogen, and argon. Both the shape and half width are significantly changed in the transition of liquid solution to solid solution, while the band position is not appreciably altered in the phase change. (Changes were not observed for the methane-argon system [17].) The recent theory of Buckingham as well as the earlier theory ascribed to Kirkwood, Bauer, and Magat have been found not to apply to these systems. No explanation is apparent for the two overlapping bands observed for carbon monoxide in the clear crystalline argon solid. The explanation of Vu et al. [4] implies that a combination band involving the fundamental band and a lattice mode is more intense than the respective fundamental. This explanation is not consistent with the observation of one band for the  $\nu_3$  vibration of methane in a clear crystalline argon solid [17]. The variation of the half width of the 0-2 band of CO in liquid oxygen in the temperature range of 57 to 82 °K cannot be readily explained with existing theories.

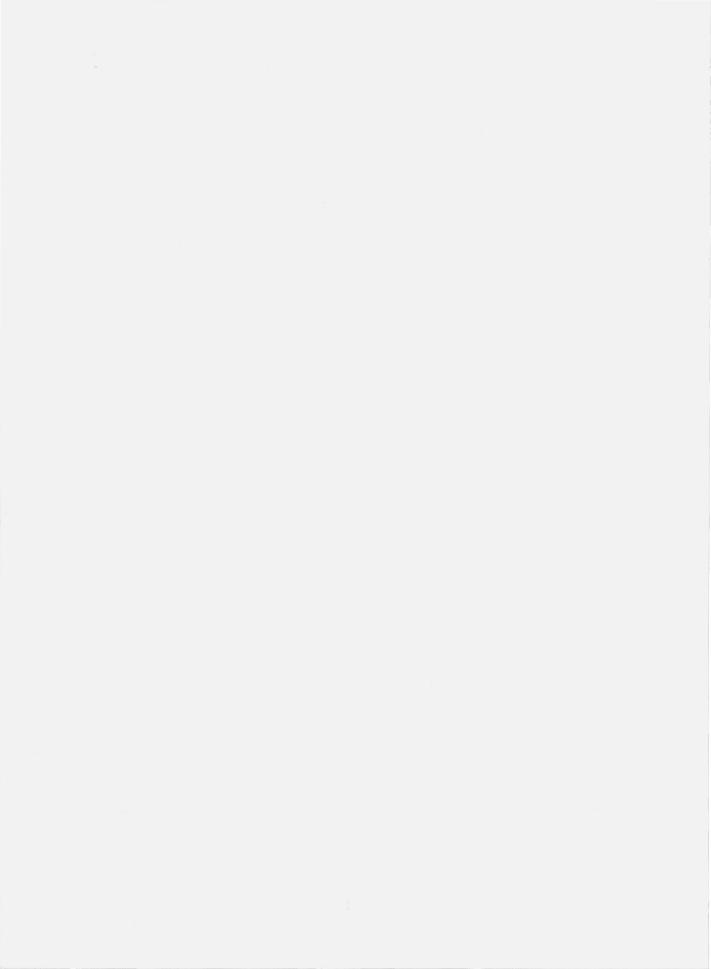
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### Publications of the National Bureau of Standards\*

### Selected Abstracts

Fringe pattern of an oscillating Fabry-Perot interferometer, K. D. Mielenz, J. Res. NBS 68C (Eng. and Instr.), No. 2, 73-82 (Apr.-June 1964).

The dependence of the fringe pattern of an oscillating Fabry-Perot interferometer upon the vibration amplitude is discussed experimentally and theoretically. If the fringes of the stationary interferometer are wide, the fringe pattern tends to disappear at certain values of the amplitude. If the stationary fringes are narrow, a splitting of fringes occurs at certain amplitudes. In both cases, the stationary pattern reappears, with reduced contrast, at intermediate amplitudes. The practicability of using these effects for the measurement of vibration amplitudes is discussed.

Mean electron density variations of the quiet ionosphere No. 12, February 1960, J. W. Wright, L. R. Wescott, and D. J. Brown, NBS Tech. Note 40–12 (Dec. 6, 1963), 35 cents. The CRPL has initiated a program for large-scale computation of electron density profiles from ionospheric vertical soundings. Scaling is performed at field stations, permitting computation of hourly profiles at the Central Laboratory. These profiles are combined to form hourly mean quiet profiles for each station and month. The results of this program for the month of February are illustrated graphically. This report is the twelfth of a series illustrating the electron density variations in the mean quiet ionosphere between latitudes 15° N and 50° N along the 75° W meridian.

## A technique for extrapolating the 1 kc values of secondary capacitance standards to higher frequencies, R. N. Jones, NBS Tech. Note 201 (Nov. 5, 1963) 15 cents.

*NBS Tech. Note 201 (Nov. 5, 1963), 15 cents.* A simple technique is described for extrapolating the 1 kc values of certain two-terminal capacitors to higher frequencies without incurring serious losses in accuracy. The method is intended for use with air capacitors having binding post or banana plug type connectors. Because of inherent errors, such connectors are not appropriate for measurement where the highest accuracy is required. For this reason, it is recommended that calibration of this type be performed by secondary laboratories and not be submitted to the National Bureau of Standards.

# Thermodynamic property values for gaseous and liquid carbon monoxide from 70° to 300 °K with pressures to 300 atmospheres, J. G. Hust and R. B. Stewart, NBS Tech. Note 202 (Nov. 30, 1963), 60 cents.

The internal energy, entropy, enthalpy, and density of carbon monoxide are tabulated as functions of pressure and temperature from 70 to 300 °K and 0.1 to 300 atmospheres. A compressibility factor-pressure chart and a temperatureentropy chart are also included. The P- $\rho$ -T values have been calculated using the Su principle of corresponding states with nitrogen as a model. Extensive comparisons are included, illustrating the deviations of the calculated values from the experimental data and from other correlated data. Equations representing the P- $\rho$ -T surface and the vapor pressure are given.

A low-pressure arc source for the emission spectrum of the FeO molecule, R. K. Dhumwad and A. M. Bass, *Appl. Opt.* 2, No. 12, 1335 (Dec. 1963).

The emission spectrum of FeO has been produced without interference from atomic iron lines. The source for this spectrum is described.

Dissociative ionization of  $H_2$ ; A study of angular distributions and energy distributions of resultant fast protons, G. H. Dunn and L. J. Kieffer, *Phys. Rev.* **132**, *No.* 5, 2109–2117 (*Dec.* 1, 1963).

Protons with energies between 2 ev and 14 ev have been observed from dissociative ionization of  $H_2$  using a rotatable collision chamber in conjunction with a small 60 sector magnetic spectrometer, and using electrons with energies ranging from threshold to 1500 ev. The degree of anisotropy and its electron energy dependence on measurements of cross sections and the energy distribution of protons is investigated. The energy distribution of protons is measured as a function of electron energy, and quite good agreement is found with predictions of the Franck-Condon principle. This is in rather sharp contrast with results of previous investigators.

First-order phase transition in a gas of long thin rods, R. Zwanzig, J. Chem. Phys. **39**, No. 7, 1714–1721 (Oct. 1, 1963). Onsager's prediction of a first order phase transition in a gas of long thin rods is verified by extensive calculations on a simple model. The molecules are rectangular parallelopipeds, of length l and square cross section  $d \times d$ . The long molecular axes can point in only three mutually perpendicular directions. Virial coefficients, up to the seventh, are calculated exactly as functions of orientation, in the limit  $l \to \infty$ ,  $d \to 0$ , and  $l^2d = \text{constant}$ . The transition predicted by Onsager's theory, based on a second virial approximation to the potential of mean force in the space of relative orientations, is observed also when all virial coefficients up to the seventh are included. The virial expansion appears to converge usefully in the vicinity of the transition.

Gamma irradiation of polytetrafluoroethylene in chlorine, R. E. Florin and L. A. Wall, *SPE Trans.* **3**, *No.* 4, 290–299 (Oct. 1963).

In chlorine polytetrafluoroethylene, irradiated in halogen atmospheres, decrease in ultimate tensile strength and elongation at break almost as rapidly as in oxygen. The rate of degradation is approximately independent of chlorine pressure down to about 1 mm Hg. The phenomena can be explained semiquantitatively in terms of first order, cage reactions of scission, recombination, and reaction with chlorine, complicated by diffusion at low pressures. However, all reaction and diffusion parameters must shift with gradual increase of crystallinity.

For a given decrease of elongation at break, polytetrafluoroethylene irradiated in a vacuum retains a relatively higher ultimate tensile strength. In the copolymer of tetrafluoroethylene and hexafluoropropylene, the changes in ultimate tensile strength and elongation at break are much slower under all conditions. Both polytetrafluoroethylene and the copolymer retain appreciable tensile strength but little elongation up to a dose of  $2 \times 10^{\circ}$ r.

The validity of crystal field theory as applied to rare earth ions: An analysis of the spectrum of praseodymium trichloride, J. C. Eisenstein, Low Symposium on Paramagnetic Resonance I, 253-260 (Academic Press, Inc., New York, N.Y., 1963).

The spectrum of  $PrCl_3$  below 25,000 cm<sup>-1</sup> is analyzed from the point of view of crystal field theory. Coulomb, spinorbit and crystal field interactions are taken into account. The Coulomb integrals, the spin-orbit coupling constant and the quantities  $A_{l}^{m}(r^{l})$  which characterize the crystal field are treated as parameters. The eigenvalue problem for the  $f^2$  configuration is solved by diagonalization of the complete interaction matrices.

The calculated positions of the energy levels are compared with the experimental results. This comparison indicates the existence of appreciable interaction between the  $f^2$  and higher configurations. Also it appears that no single set of crystal field parameters will give good agreement between calculated and observed levels for all multiplets. This difficulty may also be ascribable to neglect of configuration interaction.

**Kinetics of desorption. III. Rb**<sup>+</sup>, **K**<sup>+</sup>, **and Na**<sup>+</sup> **on rhenium**, M. D. Scheer and J. Fine, J. Chem. Phys. **39**, No. 7, 1752–1755 (Oct. 1, 1963).

The mean adsorption lifetimes  $(\tau_3)$  of Rb<sup>+</sup>, K<sup>+</sup>, and Na<sup>+</sup> ions on a clean polycrystalline rhenium surface have been measured in the millisecond region as a function of temperature under conditions of very low surface coverage. The results of these measurements are given by

Rb<sup>+</sup>: 
$$\tau_3 = (0.8 \pm 0.3) \times 10^{-13} \exp \left[\frac{26,400 \pm 350}{T}\right] \sec,$$
  
1000 < T < 1250 °K;

 $\mathrm{K}^+\!:\tau_3\!=\!(1.0\pm0.3)\!\times\!10^{_{-13}}\exp\left[\frac{27,000\pm350}{T}\right]\mathrm{sec},$  $1050 < T < 1260 \,^{\circ}\text{K}$ :

$$\begin{split} \mathrm{Na^{+}:} & \tau_{3} \!=\! (0.2 \pm 0.1) \!\times\! 10^{-13} \exp\left[\frac{31,\!900 \pm 300}{T}\right] \mathrm{sec}, \\ & 1160 \! < \! T \! <\! 1400 \, ^{\circ} \mathrm{K}. \end{split}$$

The interaction of the alkali ion with the metal surface was described by a one dimensional potential function of the form  $V(x) = l_{+} \left[ 1 + \frac{1}{m-1} \left( \frac{r_e}{x} \right)^m - \frac{m}{m-1} \left( \frac{r_e}{x} \right) \right]$  where x is the perpendicular distance of the adsorbed ion from the surface and  $l_{+}$  is the observed desorption energy. By choosing the Pauling ionic radii  $r_i$  as the distance of closest approach to the surface for an ion with energy  $l_+$  the parameters m and  $r_e$ were calculated for each alkali ion. It was found that the values of m increase and  $(r_e - r_i)$  decrease as the atomic number of the alkali ion increases.

The reactions of methyl radicals in the solid-, liquid-, and gas-phase photolysis of dimethylmercury, R. E. Rebbert and P. Ausloos, J. Am. Chem. Soc. 85, No. 20, 3086-3089 (Oct. 20, 1963).

The gas-phase photolysis of  $CD_3COCD_3$  has been investi-gated in the presence of  $CH_3HgCH_3$  from 376° to 453 °K. From the isotopic distributions of the methane and ethane fractions, evidence was obtained for the occurrence of the reaction:

#### $CD_3 + CH_3HgCH_3 - CD_3HgCH_3 - CH_3$

 $(E_{act}=12.6 \text{ kcal/mole})$ . This reaction is also postulated to occur in the liquid-phase photolysis of dimethyl mercury. From the isotopic distribution of the ethane produced in the liquid—and solid-phase photolysis of CH<sub>3</sub>HgCH<sub>3</sub>-CD<sub>3</sub>Hg  $CD_3$  mixtures, it was concluded that cage recombination of methyl radicals does take place. Contrary to the conclu-sions reached in an earlier work by Derbyshire and Steacie, no evidence could be obtained for hot methyl radical effects in the liquid-phase photolysis of dimethyl Mercury.

Radiation-induced polymerization at high pressure of ntetradecafluoroheptene-1; 1,1,2-trifluorovinyl phenyl ether; and 1,2,3,4,5-pentafluorophenyl 1,1,2-trifluorovinyl ether, D. W. Brown and L. A. Wall, SPE Trans. 3, No. 4, 300-308 (Oct. 1963)

The radiation-induced polymerization of n-tetradecafluoro-heptene-1 was investigated at pressures of 8,100, 11,900, and 17,100 atmospheres and temperatures between 90 °C and 267 °C. Both the rate of polymerization and the molecular weight of the polymer first increase and then decreases as temperature is increased at constant pressure. The maximum number-average molecular weight was 28,000. The data are interpreted in terms of a free radical mechanism. The polymer has a low ceiling temperature. As temperature is increased the depropagation step becomes important and reduces the rate of polymerization. Under some conditions transfer seems to be a significant part of the mechanism.

Several radiation-induced polymerizations at high pressure were carried out with 1,1,2-trifluorovinylphenyl ether as well as one with 1,2,3,4,5-pentafluorophenyl 1,1,2-trifluorovinyl ether. The results suggest transfer limits the molecular weight of the polymers.

On the growth of helical dislocations, R. deWit, Trans. Met. Soc. AIME 227, 1443–1452 (Dec. 1963).

Conclusions reached in a paper by Weertman are amplified in a mathematical and graphical way. It is shown that in a stressed crystal a straight dislocation may be in a position of unstable equilibrium with respect to helix developof an analysis of a small perturbation may start the dislocation off on its helical path. Helix development occurs by diffusion; bulk diffusion is necessary for development from a screw, but core diffusion is sufficient for development from an edge dislocation. For a mixed dislocation helix development can take place by core diffusion if the helix also climbs; a diffusion reversal takes place when the slope of the helix equals the slope of the Burgers vector. The work done on a crystal by the external forces is graphically shown to be con-sistent with the direction of motion of the dislocation in helix development. Finally a detailed mechanism for tangle formation from helices is presented. In the course of helix development a glide situation may be reached where a segment of each helix loop lies in a slip plane in which it can expand by glide. Thus it is visualized how a helix can deteriorate into a tangle.

A study of anthracene fluorescence excited by the ruby giant pulse laser, J. L. Hall, D. A. Jennings, and R. M. McClintock, *Phys. Rev. Letters* 11, No. 8, 364–366 (Oct. 15, 1963).

The unfocused red output light of a ruby Q switched laser has been used to excite blue fluorescence in single crystals of anthracene. The intense normal singlet fluorescence coincident in time with the laser pulse is attributed to two-photon processes. Second harmonic generation and reabsorption is ruled out on the basis of the measured low SHG efficiency of anthracene for the 1.06 micron output of neodymium glass Q switched laser. In addition, a much weaker blue fluorescence is still observable milliseconds after the giant laser pulse. This delayed fluorescence is consistent with bimolecular recombination of triplet excitons. Numerical values are obtained for the four parameters of the model which describes the observed fluorescence.

Knight shifts and line widths of the nuclear magnetic reso-

nance of  $\mathbf{Pb}^{207}$  in lead-indium alloys, R. J. Snodgrass and L. H. Bennett, *Phys. Rev.* **132**, 1465–1474 (Nov. 15, 1963). The nuclear magnetic resonance of  $\mathbf{Pb}^{207}$  was observed and accurately measured at room temperature and 77° K, in pure lead metal powder and in a series of lead-indium alloy powders read metal powder and in a series of lead-indium alloy powders containing up to 75% indium. Upon the addition of indium, the central frequency of the Pb<sup>207</sup> absorption line increases by a small fraction of the line width. At 5 Mc/sec, this frequency shift between pure lead and 20 at. % In is 800 cps, compared to a linewidth of 18 kc/sec in the 20 at. % In sample. The increase in frequency is also a small fraction of the Knight shift Ak/k=1.3% up to 20 at % In . In the sample. The increase in frequency is also a small fraction of the Knight shift,  $\Delta k/k=1.3\%$  up to 20 at. % In. In the cubic lead phase, the frequency shift is linear with composi-tion. From the temperature dependence of the linewidth,  $T=2.6\times10^{-1}$ the spin-lattice relaxation time is found to be  $T_1 = 3.6 imes 10^{-4}$ sec at 77° K. The absorption linewidth increases rapidly upon alloying, due to a combination of indirect spin exchange and pseudo-dipolar coupling. The line shape changes from Lorentzian to Gaussian. A second moment analysis yields a value for the near-neighbor exchange constant  $h^{-1}|A|=2.5$ kc/sec. The pseudo-dipolar exchange constant is found to be  $h^{-1}|B|=1.1$  kc/sec. The relatively large value of 0.4 for the ratio BA<sup>-1</sup> indicates that the amount of p-character probably exceeds the amount of s-character in the electron wave func-tions at the Fermi surface in this alloy. Volume effects which are comparable to the observed change in Knight shift preclude the possibility of confirming or denying the existence of charge oscillations of the type discussed by Friedel and others.

#### Calculations of the potential and effective diffusion constant in a polyelectrolyte solution, S. R. Coriell and J. L. Jackson, J. Chem. Phys. 39, 2418 (1963).

Numerical computations of the electrostatic potential and the effective diffusion constant of counterions in a periodic polyelectrolyte solution are reported. Some results for the potentials for various polyion charge densities and polyion sizes are presented graphically. The calculated diffusion constants are compared with experimental data on the diffusion of labeled sodium ions in polyacrylic acid-sodium hydroxide solutions as well as with the earlier approximate calculations Recalibration of NBS standards of spectral transmittance, H. J. Keegan, J. C. Schleter, and M. A. Belknap, J. Opt. Soc. Am. 54, No. 1, 69-74 (Ja v. 1964).

In 1934, Gibson, Walker, and Brown developed sets of four colored glass filters to serve as working standards of spectral transmittance for checking the reliability of spectrophotometers. Several sets of these glasses were measured care-fully and reserved and designated as future reference standards. Duplicate standards evaluated by comparison with the reference standards are available by purchase to the public. The current set of reference standards was established in the years 1945 to 1947, and one of these reference standards (selenium-red) was recalibrated in 1952. This paper reports a recalibration, made in 1961 and 1962, of all four glasses (selenium-red, carbon-yellow, copper-green, cobalt-blue) on three spectrophotometers (Cary 14, Beekman DU, König-Martens). Except for the cobalt-blue standard, the values of spectral transmittance found differ from those previously assigned by amounts differing at some wavelengths by as much as or slightly more than the uncertainties estimated for the present values, though not by amounts exceeding the combined uncertainties of the present and previous determinations. The indicated changes for these three standards are fairly regular, however, and support the view that the selenium-red and carbon-vellow standards are changing chiefly by formation of a reflectance-reducing film on the surfaces. The indicated rate of upward drift is slow, and suggests that it takes about 10 years for the drift to exceed the assigned uncertainty.

## Surface flammability measurements by the radiant-panel method, A. F. Robertson, Am. Soc. Testing Mat. Spec. Tech. Publ. **344**, 33-46 (1962).

It is suggested that the flammability of solids may be considered as a function of the ratio of heat release rate to critical ignition energy of the material being studied. Based on this concept, the radiant-panel flammability test method has shown its usefulness as a research tool. A review is included of previous studies made by use of this method.

Recently obtained experimental data are presented which illustrate the large changes in flammability which can occur with changes of the relative humidity of the ambient conditioning atmosphere. Data are presented which suggest that the subsurface heat-dissipation behavior of the material under test may have an important influence on flammability.

The paper concludes with the suggestion that, although the radiant panel flammability test method has achieved some recognition, it would be a mistake to assume that it, or any other test method, would be ideal for prediction of the surface flammability hazard of all materials in all situations.

#### Stress-strain relationships in yarns subjected to rapid impact loading. Part X: Stress-strain curves obtained by impacts with rifle bullets, J. C. Smith, C. A. Fenstermaker, and P. J. Shouse, Textile Res. J. 33, 919–934 (Nov. 1963).

P. J. Shouse, Textile Res. J. **33**, 919–934 (Nov. 1963). When a yarn is struck transversely, a V-shaped wave of transverse motion is caused to spread outwards at a velocity  $\bar{U}$  depending upon the impact velocity V. In this research data on  $\bar{U}$  vs V for impact velocities between 10 m/sec and 700 m/sec are analyzed to determine stress-strain behavior in high-tenacity nylon and polyester yarns. The data are obtained by shooting rifle bullets at a yarn and recording the resulting configurations by microflash photography. A strain-rate-independent theory for transverse impact behavior is used to calculate stress-strain data.

It was found that the time required to break a yarn depended upon the impact velocity. Nylon yarns broke 10  $\mu$ sec after impact at 650 m/sec with a calculated breaking strain of 10.0% and tenacity of 77 g/tex. At 495 m/sec velocity the yarn broke within 100  $\mu$ sec at 7.4% strain and 52 g/tex tenacity. The corresponding values in polyester yarn were, for a 10- $\mu$ sec break, 620 m/sec, 10.5%, and 67 g/tex; for a 100- $\mu$ sec break, 420 m/sec, 6.5%, and 40 g/tex.

Wavelength of Hg<sup>198</sup> Zeeman filter relative to that of the 2537-A absorption line of an atomic beam, W. G. Schweitzer, Jr., and K. G. Kessler, J. Opt. Soc. Am. 53, No. 12, 1382–1388 (Dec. 1963).

We have made a precise comparison of the wavelength passed by a Hg<sup>198</sup> Zeeman filter with that of the 2537–Å absorption line of an atomic beam. This was done by passing the light from the filter through the atomic beam and then comparing the amplitudes of the two peaks in the resulting reversed lines. A calibration was obtained by measuring the ratio of peak amplitudes with the beam tilted at various angles to the optic axis so as to introduce known Doppler shifts. The wavelengths of the Zeeman filter and atomic beam are shown to be equal to about one part in 10<sup>9</sup>.

Numerical solutions of the convolution-hypernetted chain integral equation for the pair correlation function of a fluid. I. The Lennard-Jones (12, 6) potential, M. Klein and M. S. Green, J. Chem. Phys. **39**, No. 6, 1367-1387 (Sept. 15, 1963).

The integral equation of the convolution-hypernetted chain approximation is solved numerically at five temperatures for the Lennard-Jones (12, 6) potential. Due to an inconsistency in the approximation there are two equations of state associated with it. These are compared with each other, with other theories, and with the experimental argon equation of state. At high temperatures, the two equations of state agree both with experiment and with more a priori theory at low densities and bracket them at higher densities, their mean giving a good representation of both. The integral equation is found to be singular at certain temperature-density points, their locus forming a dome shaped curve in the  $T-\rho$  plane. These points are shown to correspond to the limits of metastability in the van der Waals gas, the highest temperature point being the critical point. The nonsingular points below the critical point correspond either to a homogeneous gas (low densities) or liquid (high densities) phase. The former are in good agreement with the three-term virial series, as expected, and the latter are a considerable improvement over it. The equation of state is a considerable improvement over that obtained from the Born-Green equation by Kirkwood, Lewinson, and Alder, the latter predicting negative pressures over most of the liquid range while these results show only positive pressures. The comparisons with experiment are obscured by the inadequacy of the (12, 6) potential function. The use of temperature "compensated" potential parameters (as determined by the second virial coefficient) indicates that the use of a more reasonable potential function in the theory will give a relatively good representation of the equation of state of a a fluid over a wide range of temperatures and densities.

## The three-body scattering operator in nonequilibrium statistical mechanics, J. Weinstock, *Phys. Rev.* 132, *No.* 1, 470–482 (Oct. 1, 1963).

A method is presented for calculating the time dependent irreducible clusters— $\beta_s(t)$ —which appear in the kernel of the equation of evolution derived in the preceding article. The clusters  $\beta_1(t)$  and  $\beta_2(t)$ —which correspond to binary and ternary collisions, respectively-are calculated in detail. They are each found to divide into the two following parts: (1) a "completed" collision part which corresponds to those collisions completed before time t, and (2) an "incompleted" part which corresponds to those collisions not completed by time t. The incompleted collision parts contribute to the "memory" of the equation of evolution and are shown to be relatively small when t is large. The completed collision parts, which play a central role in the theory of transport coefficients, are time independent scattering operators in momentum space and do not contribute to the memory. By means of the "binary collision expansion" a systematic method is presented for the calculation of the three-body scattering operator [lim  $t^{-1}\beta_2(t)$ ] which is directly applicable  $t \rightarrow$ 

to interaction forces with infinite repulsions. An approximate formula is then derived for this scattering operator in a form which can be readily used to calculate the density correction to transport coefficients which arises from ternary collisions.

Macro-pores in leather as determined with a mercury porosimeter, J. R. Kanagy, J. Am. Leather Chemists Assoc. LVIII, No. 9, 524–550 (Sept. 1963).

A study was made of the pore structure in leather and in other

porous materials with a mercury porosimeter at absolute pressures ranging from 5 to 3000 psi. Pore radii correspond-ing to these pressures vary from 50 to 0.04 microns. This range is referred to as the macro-pore range. Leather and other natural collagenous materials were compared to microporous plastics and fritted-glass discs. The results indicate that a characteristic pore structure giving rise to many different-sized pores related to the fibrous structure exists in leather, whereas the pores in manufactured materials which are designed for a specific use are more uniform in size. A differential analysis of the integral volume-pressure curves indicates that a large part of the pore volume of collagenous materials in the form of hides occurs at radii of 5 to 0.5 microns. For rat tail tendons, a large fraction of the pore volume exists for pores in close proximity to this, 2.5 to 0.5 microns. The pores which constitute these volumes are believed to exist between the primitive fibers. The volume from pores smaller than 0.25 micron in radius very probably are within the fibril region.

#### Cluster formulation of the exact equation for the evolution of a classical many-body system, J. Weinstock, Phys. Rev. 132, No. 1, 454-469 (Oct. 1, 1963).

An exact non-Markoffian equation is derived for the evolution of an infinite homogeneous system. This equation-which may be viewed as a time dependent analogue of the equilibrium virial expansion—may be readily applied when the forces between particles include infinite repulsions. The forces between particles include infinite repulsions. derivation of this equation from Liouville's equation is analogous to Mayer's derivation of the virial expansion from the partition function. Fourier expansions and expansions in powers of the interaction potential are avoided by dealing with s-body Green functions (propagators) which are always convergent functions of the interaction potential. These functions correspond to multiplet collisions in ordinary configuration space and are time dependent analogues of the irreducible clusters well-known in equilibrium statistical mechanics.

The kernel (memory) of the equation of evolution consists of a linear sum of the time dependent irreducible clusters. The non-Markoffian behavior of the equation of evolution is. thus, directly given by the time dependence of these clusters, and is explicitly related to incompleted collisions. The equation of evolution is solved in the asymptotic limit of long times. In this limit it is found (because the kernel rapidly vanishes) that the equation reduces to a Markoffian master equation involving a scattering operator for both completed and incompleted collisions in configuration space.

### An analysis of pressure and stress distribution under rigid Bridgman-type anvils, J. W. Jackson and M. Waxman, Book, High-Pressure Measurement, pp. 39–58, ed. Giardini and Lloyd (Butterworth, London, England, 1963).

Analytical expressions are derived for the pressure and stress distribution in a short cylinder compressed by Bridgman type anvils, assuming the anvils to be rigid plates. The short cylinder is considered to be composed of an inner cylinder bound by an outer shell. The deformation for each may be elastic or plastic.

### Interaction energies and transport coefficients of Li+H and O+H gas mixtures at high temperatures, P. H. Krupenie, E. A. Mason, and J. T. Vanderslice, J. Chem. Phys. **39**, No. 10, 2399-2408 (Nov. 15, 1963).

Accurate potential energy curves for the  $X^1 \Sigma_{q}^+$ ,  $A^1 \Sigma_{u}^+$ ,  $B^1 \Pi_{u}$ , and  $C^1\Pi_u$  states of the Li<sub>2</sub> molecule are calculated from observed spectroscopic data by the method of Rydberg-Klein-Rees (RKR), and compared with previous quantummechanical calculations. Long-range attractive potentials are estimated by extrapolation of functions fitted to the RKR ground-state curves of  $Li_2$ , LiH, and OH. From these, the repulsive potentials derivable from interacting ground-state atoms are estimated semiempirically. Cellision integrals computed from the potentials, and transport coefficients of the gaseous systems Li+Li, Li+H, and O+H are calculated for temperatures of 1000 to 10,000 °K.

A surprising result is the extraordinarily large values of the collision integrals for Li + Li (and Li + H) interactions, which result in unexpectedly small values of diffusion coefficient, viscosity and thermal conductivity. For traces of Li in Li+H mixtures at low temperature, the thermal diffusion factor is very large. Various approximate formulas for viscosity and thermal conductivity of mixtures are seen to give poor agreement with exact calculations for the systems considered.

Inertial effects in the phenomenological theory of thermal diffusion in liquids, R. E. Nettleton, Il Nuovo Cimento 28, Serie X, 952–969 (Dec. 7, 1962).

The energy flux carried by diffusing molecules in a binary liquid solution is shown to obey a rate equation linking its time rate of change to energy-exchange and particlescattering terms and to driving terms proportional to the temperature and concentration gradients. This equation together with a similar equation for the energy flow carried by high-frequency sound waves, is written in terms of thermodynamic forces which are assumed linear in the two heat flux components, and it is found that these forces may be calculated by interpreting the rate equations as ther-modynamic phenomenological relations and then applying Onsager's theorem and Maxwell's relations. From the forces, one can determine explicitly the dependence of the free energy per molecule A on the energy flux vectors and, in the limit of low acoustic frequencies, the dependence of A on the square of the concentration gradient. The low-frequency limits of the rate equations also give an expression for the thermal diffusion coefficient.

### Mass spectra and metastable transitions of H<sub>2</sub>S, HDS, and D<sub>2</sub>S, V. H. Dibeler and H. M. Rosenstock, J. Chem. Phys. 39, No. 11, 3106-3111 (Dec. 1, 1963). Mass spectra are reported for isotopic hydrogen sulfides.

The occurrence of metastable transitions and the effect of isotopic substitution on the relative abundance are discussed. Appearance potential are given for the molecule and fragment ions in  $H_2S$ , the molecule ions of HDS and  $D_2S$ , and the principal metastable transition in each species. The latter process is interpreted as resulting from electronic transitions rather than from vibrational relaxation processes.

### Spectrum of Nd<sup>3+</sup> in LaCl<sub>3</sub>, J. C. Eisenstein, J. Chem. Phys.

**39**, No. 9, 2134-2140 (Nov. 1, 1963). The energy levels of the Nd<sup>3+</sup> ion in LaCl<sub>3</sub> are calculated by finding the eigenvalues of the matrices for the combined Coulomb, spin-orbit and crystal field interactions within the  $f^3$  configuration. By judicious choice of the three Slater integrals and the spin-orbit coupling constant the standard deviation between the calculated and the experimental posi-tions of 21 terms can be reduced to  $93 \text{ cm}^{-1}$ . Crystal field parameters can be chosen which vield a standard deviation of  $0.90 \text{ cm}^{-1}$  between the calculated and the measured splittings of 31 levels in 7 terms. The calculated Zeeman splitting factors in the direction parallel to the crystal axis are in good agreement with the measured values.

### Two assumptions in the theory of attractive forces between long saturated chains, R. Zwanzig, J. Chem. Phys. 39, No. 9, 2251–2258 (Nov. 1, 1963).

A recent calculation by Salem of the attractive forces between two long parallel hydrocarbon chains was based on two assumptions: (1) local pairwise additivity of dispersion forces between individual groups on each chain, and (2) local isotropy of the polarizability of a group on the chain. The validity of these assumptions is assessed here by means of a Drude model calculation of the interaction between two parallel linear lattices of dispersion oscillators. We conclude that the assumptions are not valid, because of strong induced dipole interactions between neighbors along the chain. Salem's numerical results are essentially correct, however, due to use of an experimentally determined bond polarizability at a crucial stage of the calculation. This allowed for the effects of interactions between neighbors.

### Binary mixtures of dilute bose gases with repulsive inter-actions at low temperatures, D. M. Larsen, Ann. Phys. 24, 89-101 (Oct. 1963).

This work is a theoretical investigation of the behavior of mixtures of two species of bosons with repulsive interactions at temperatures in the neighborhood of absolute zero. Using the Bogoliuboy approximation and a novel canonical transformation we investigate the excitation spectra, ground state energy, excitation wave functions, and ground state pair correlation function of the mixture, valid for interactions of short range, in the low density limit.

A criterion for phase separation is given and varified thermodynamically for the case in which the interactions among the particles can be replaced by the two body S-wave pseudopotential. It is shown that two dilute hard sphere bose gases of different mass do not mix in any proportions at absolute zero.

## Statistics of irreversible termination in homogeneous anionic polymerization, B. D. Coleman, F. Gornick, and G. Weiss, J. Chem. Phys. **39**, No. 12, 3233–3239 (Dec. 15, 1963).

The effect of irreversible termination on the molecular weight distribution of a polymer prepared by homogeneous anionic polymerization is examined for cases in which the initiator is monofunctional and initiation is instantaneous. A general procedure for the calculation of the chain length distribution, as well as its moments, is presented. The procedure is then illustrated by an exact treatment of an isothermal batch polymerization for which we obtain the ratio  $r_{\sigma}(t)$  of the weight to number average molecular weights as a function of the fraction of monomer consumed, the ratio  $\sigma$  of the initial terminator concentration to that of the initiator, the ratio  $\rho$  of the rate constant for termination to the rate constant for propagation, and the average degree of polymerization at time  $t, \bar{m}^1(t)$ .

When  $\sigma$  is much less than unity, and the limiting number average D.P.  $\overline{n}^{1}(\infty)$  is very large,  $r_{\sigma}(t)$  approaches the following value as the reaction nears completion:  $r_{\sigma}(\infty) = 1 + \sigma \rho$  $(2+\rho)^{-1}$ .

#### The structure of gaseous copper (II) nitrate as determined by electron diffraction, R. E. LaVilla and S. H. Brauer, J. Am. Chem. Soc. 85, 3597-3600 (Nov. 1963).

Anhydrous copper nitrate has a sufficient vapor pressure at 180–200 °C to permit the recording of electron diffraction photographs. That this gas is monomeric has been demonstrated by Addison, *et al.*, by means of vapor density measurements and confirmed with mass spectrometry; its range of stability has also been ascertained.

Visually estimated intensities were used for the inversion to a radial distribution, and were compared with computed intensity curves for many models. The analysis indicates the molecular structure of gaseous copper nitrate to be of the bidentate form with the copper atom occupying the center of inversion. The central copper atom has four nearest oxygen atoms at 2.00  $\pm 0.02$ Å, and two Cu-N distances of 2.30  $\pm 0.03$ Å,  $< \text{O-N-O} = 120^{\circ} \pm 2^{\circ}$  and < O-Cu- $O \approx 70^{\circ}$ . The errors shown are mean deviations.

Spectrum of  $Er^{3+}$  in LaCl<sub>3</sub>, J. C. Eisenstein, J. Chem. Phys. **39**, No. 9, 2128-2133 (Nov. 1, 1963). The energy levels of the  $Er^{3+}$  ion in LaCl<sub>3</sub> are calculated by

The energy levels of the  $Er^{3+}$  ion in LaCl<sub>3</sub> are calculated by finding the eigenvalues of the matrices for the combined Coulomb, spin-orbit and crystal field interactions within the  $f^{11}$  configuration. For suitably chosen values of the three Slater integrals and the spin-orbit coupling constant the root-mean-square (rms) deviation between the calculated and the experimental positions of 20 terms is 140 cm<sup>-1</sup>. Crystal field parameters can be chosen which reduce the rms deviation between the calculated and the measured splittings of 72 levels to 3.84 cm<sup>-1</sup>. Zeeman splitting factors in the direction parallel to the crystal axis are also calculated. The results for  $Er^{3+}$  in LaCl<sub>3</sub> are compared with those for Nd<sup>3+</sup> in LaCl<sub>3</sub>.

## Large-angle inelastic scattering of 500-kev electrons. J. W. Motz and R. C. Placious, *Phys. Rev.* 132, *No. 3*, 1120–1122 (*Nov. 1*, 1963).

Experimental results are given for the energy spectra of electrons inelastically scattered at 100 degrees, with 500 kev electrons incident on thin targets of gold and of aluminum. This large angle inelastic scattering arises primarily from the two processes of bremsstrahlung and of atomic K-shell ionization with a small contribution from double or plural scattering effects. In the 300 kev energy region for the scattered electron, the sum of the theoretical cross sections evaluated with the Born calculations of Racah and of Weber, Deck, and Mullin for the respective two processes is approximately an order of magnitude smaller than the experimental values. This disagreement can be attributed to the breakdown in this energy region of both the high energy approximation in the latter calculation and the Born approximation in both calculations.

Investigation of shallow reference cavities for high-temperature emittance measurements, D. G. Moore (Symp. Measurement of Thermal Radiation Properties of Solids, Dayton, Ohio, Sept. 5–7, 1962), Natl. Aeron. and Space Admin. SP-31, Session V, Paper 52, p. 515 (1963).

Total normal emittance measurements were made on small specimens with shallow reference holes of circular cross section. The ratio of the radiant flux density from the surface to the flux density from the hole was measured and this value then converted to emittance by a theoretical expression based on hole dimensions. The expression applies only to diffusely reflecting materials.

Measurements were made on four different diffusely reflecting materials. Specimens of oxidized nickel that had reference holes with depth-to-radius ratios of 1.7 to 3.7 gave corrected total normal emittance values at  $1350^{\circ}$  K in the range 0.85 to 0.87. The emittance of oxidized Inconel, when determined for a specimen with a reference hole having a depth-to-radius ratio of 1.7, was found to be in good agreement with values obtained by a heated strip method. The emittance measurements on four sintered alumina specimens varied from 0.43 to 0.47 when measured in air at  $1375^{\circ}$  K.

The determined emittance for a polished specimen of highpurity graphite with a shallow reference hole increased with temperature linearly from 0.59 at  $1100^{\circ}$  K to 0.74 at  $2150^{\circ}$  K. These values were in good agreement with those reported for polished graphite when measured by the rotating specimen method.

An approach to thermal emittance standards, J. C. Richmond, W. N. Harrison, and F. J. Shorten (Symp. Measurement of Thermal Radiation Properties of Solids, Dayton, Ohio, Sept. 5-7, 1962), Natl. Aeron. and Space Admin. SP-31, Sessiou IV, Paper 41, p. 403 (1963).

A double-beam ratio-recording infrared spectrometer was modified to record directly the normal spectral emittance of strip specimens that are heated by passing a current through them. A laboratory blackbody furnace and a hot specimen at the same temperature serve as sources for the respective beams. Temperature equalization is achieved by means of a differential thermocouple. Automatic data-processing equipment corrects for "zero-line" and "100%-line" errors on the basis of previously-recorded calibrations, and also computes from the spectral data, as the measurement progresses, total emittance or absorptance for radiant energy having any known spectral distribution of flux.

Broadening of the  $\nu_3$  lines of HCN due to argon, carbon dioxide, and hydrogen chloride. R. J. Thibault, A. G. Maki, and E. K. Plyler, J. Opt. Soc. Am. 53, No. 11, 1255-1258 (Nov. 1963).

The pressure broadening effect of argon, carbon dioxide, and hydrogen chloride on the  $\nu_3$  band of HCN has been measured. The broadening effects of the different gases are found to be in qualitative agreement with the theory. Of particular importance is the observation of an oscillatory behavior in the J dependence of the line half width for HCl+HCN. This oscillatory behavior is explained as due to a dipoledipole interaction for which the large difference between the rotational levels of perturber and absorber molecules causes some levels to be in resonance while others are not.

### Other NBS Publications

### J. Res. NBS 68C (Eng. and Instr.), No. 2 (Apr.-June 1964), 75 cents.

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Interferometer for testing extended surfaces such as surface plates and precision ways. J. B. Saunders and J. V. McDermott.

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#### Radio Sci. J. Res. NBS/USNC-URSI, Vol. 68D, No. 2 (Feb. 1964), \$1.00.

- Generation of an electromagnetic pulse by an expanding plasma in a conducting half-space. A. P. Stogryn and R. N. Ghose.
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Capacitor type biconical antennas. J. Galejs.

- Simulated angular response patterns for transhorizon propa-gation. J. W. Strohbehn and A. T. Waterman, Jr.
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#### Radio Sci. J. Res. NBS/USNC-URSI, Vol. 68D, No. 2 (Mar. 1964), \$1.00.

- An interpretation of rapid changes in the phase of horizontally polarized VLF waves recorded at night over a short path in the southwestern United States. E. E. Gossard and M. R. Paulson.
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Lunar semi-diurnal tides in h'F and their influence on transequatorial radio progapation. J. A. Thomas.

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- Auroral-zone observations of infrasonic pressure waves related to ionospheric disturbances and geomagnetic activity, W. H. Campbell and J. M. Young, J. Geophys. Res. **68**, No. 21, 5909–5916 (Nov. 1, 1963).
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