

Optical Constants of Metal-Ammonia Solutions*

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An ellipsometric technique has been used to determine the optical constants of sodium-, lithium-, and calcium-ammonia solutions between 0.6 and 2.3 eV in the temperature range of 213 to 233 K. The sodium-ammonia data span the range of the metal-nonmetal transition. The alkali metal solutions of concentration $x \geq 8$ mole percent metal (MPM) are clearly free-electronlike, whereas, the solutions of concentration ≤ 4 MPM strongly indicate the presence of the solvated electron. In the intermediate concentration range ($4 < x < 8$ MPM), the solutions are undergoing the metal-nonmetal transition; and the species governing the optical properties cannot be unambiguously determined, but probably involve both bound and free electrons. The temperature dependence of the optical constants of concentrated ($x \geq 6$ MPM) alkali metal-ammonia solutions was found to be negligibly small, while that of less concentrated solutions was consistent with that observed in the dilute alkali metal solutions. Concentrated solutions of calcium in ammonia (> 6 MPM) deviated considerably from the Drude model but still appeared to be free-electronlike, as evidenced by the lack of structure in the absorption. They differed somewhat from the alkali metal solutions of similar electron concentration.

I. INTRODUCTION

The present work was undertaken to determine the optical constants of several concentrated metal-ammonia solutions and their temperature dependences. The optical constants of concentrated lithium-ammonia solutions have been previously determined by Cronenwett¹ in the concentration range of 4–20 mole percent metal (MPM).² The only other optical measurements which have been reported in concentrated solutions are by Beckman and Pitzer,³ though several authors have studied dilute solutions.⁴ The optical properties of the dilute solutions in the near ir and visible part of the spectrum are due to the presence of solvated electrons.^{3,4} A solvated electron is visualized as an electron localized in a bubblelike state in the solvent due to interaction of the electron with the solvent polarization.⁵ For Li-NH₃ solutions in the concentration range of 8–20 MPM, the results for the dielectric constant $\tilde{\epsilon} = \epsilon_1 + \epsilon_2$ were found to agree qualitatively with the Drude free-electron formulas:

$$\epsilon_1 = \epsilon_\infty - \omega_P^2 \tau^2 / (1 + \omega^2 \tau^2), \quad (1)$$

$$\text{and } \epsilon_2 = \omega_P^2 \tau / \omega (1 + \omega^2 \tau^2), \quad (2)$$

where ϵ_∞ is the medium dielectric constant, ω the angular frequency of light, τ the relaxation time, $\omega_P^2 = (4\pi N_0 e^2) / m_0$ the square of the angular plasma frequency, and N_0 the density of conduction electrons. For solutions containing less than 8 MPM, the dielectric constant exhibited a marked deviation from the Drude model and gave evidence

of bound electrons.

In the present work, the investigation has been extended to sodium-ammonia, calcium-ammonia, and less concentrated lithium-ammonia solutions. The temperature dependence of the optical constants has been measured in the temperature range of 213–233 K.

The quantity $\alpha = (N^*/N_0)(m^*/m_0)^{-1} \epsilon_\infty^{-1}$ has been determined for several concentrations by evaluating the sum rule,⁶

$$\int_0^\infty d\omega \text{Im}[\tilde{\epsilon}(\omega)]^{-1} \omega = (-\frac{1}{2}\pi) \omega_P^2 \epsilon_\infty^{-1}, \quad (3)$$

which may be rewritten

$$\begin{aligned} (2\pi^2 e^2 \hbar)^{-1} \int_0^\infty \omega \epsilon_2 / (\epsilon_1^2 + \epsilon_2^2) d(\hbar\omega) \\ = (N_0 / m_0) \alpha, \end{aligned} \quad (3')$$

where $\text{Im}(\epsilon^{-1}) = \epsilon_2 / (\epsilon_1^2 + \epsilon_2^2)^{-1}$ is the energy-loss function (ELF).

The optical data substantiate previous indications of a metal-nonmetal transition⁵ at concentrations below 8 MPM and, in addition, provide information on the nature of the localized electron states.

II. EXPERIMENTAL

An ellipsometer constructed by Cronenwett¹ in the manner of Archard⁷ was used to determine the optical constants in the energy range 0.65–2.35 eV. Linearly polarized light was reflected from a quartz-solution interface, and parameters of the resulting elliptically polarized light were deter-

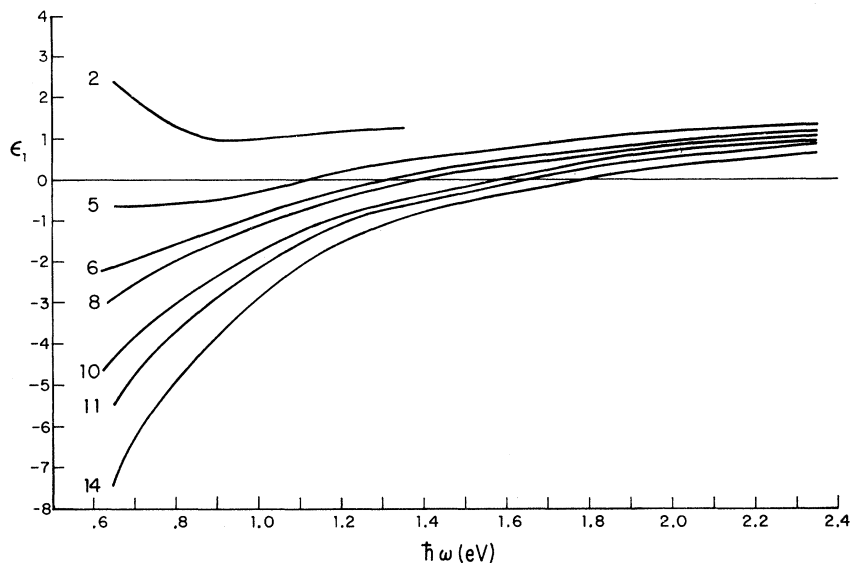


FIG. 1. Real part ϵ_1 of the dielectric constant for several sodium-ammonia solutions near 230 K as a function of photon energy. The numbers at the left-hand edge of each curve give the metal content in mole percent metal (MPM). The low-concentration curves show bound-electron effects; the high are free electronlike.

mined. The Fresnel formulas were then used to calculate the dielectric constant. Details of the experimental technique have been described elsewhere.¹ The temperature-regulating scheme, sample preparation, and cleaning procedures have been described by Kyser.⁸ Random errors are less than 4% in every case. Our only defense against the systematic errors which plague optical measurements lies in the consistency of the data, which persists over an exceedingly wide range of properties.

III. RESULTS AND DISCUSSION

Sodium-Ammonia Solutions

The real and imaginary parts of the dielectric constant and the energy-loss function are shown in Figs. 1-3. The peak in $\omega\epsilon_2(\epsilon_1^2 + \epsilon_2^2)^{-1}$, which

occurs when $\epsilon_1 = 0$, $\epsilon_2 \ll 1$, is evidence of collective (plasma) oscillations in the concentrated solutions. Values of α are calculated using the sum rule [Eq. (3')], which is independent of any particular model, and are shown in Table I. Hall-effect data^{5,8} indicate that $N^* = N_0$ in the concentrated solutions, and, therefore, the values of α are believed to reflect $\epsilon_\infty(m^*/m_0) = 2$. If ϵ_∞ is taken as unity, the effective mass ratio is in qualitative agreement with magnetic-susceptibility data.⁹ There is little evidence for any concentration effects on α above 8 MPM.

The data were first compared to the Drude model. The background dielectric constant ϵ_∞ has been assumed to be unity in the determination of the optical relaxation time $\tau_{\text{opt}} = (\epsilon_\infty - \epsilon_1)/\omega\epsilon_2$, and in the Drude model calculations for all metal-ammonia solutions studied. Results for τ_{opt} are sensitive to the value of ϵ_∞ and a discussion of the

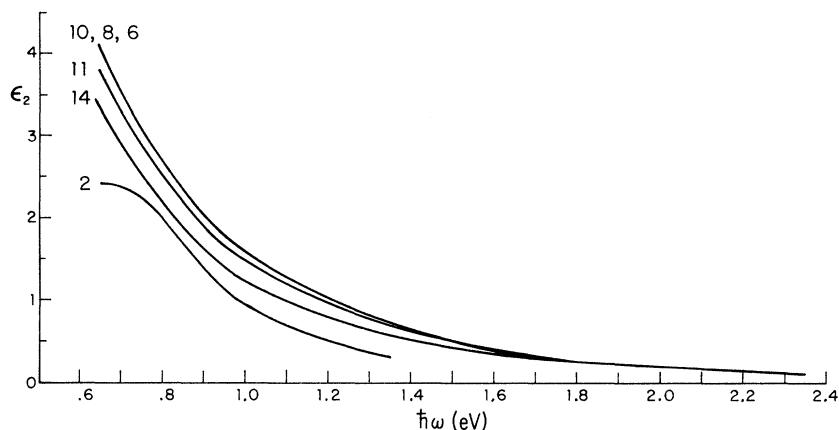


FIG. 2. Imaginary part ϵ_2 of the dielectric constant for the same solutions as Fig. 1.

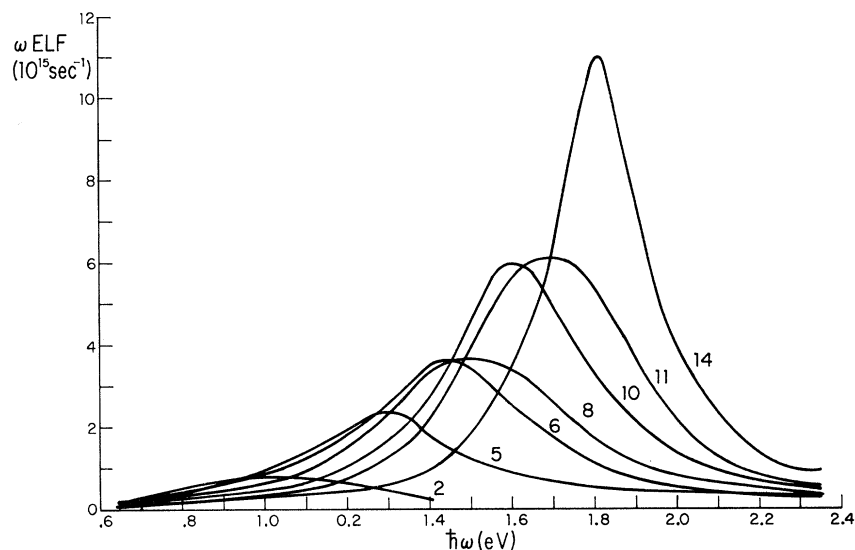


FIG. 3. Energy-loss function (ELF) (times frequency) calculated from the data of Figs. 1 and 2. The peak is indicative of a plasma resonance, and the area under the curve is related to the density and effective mass of the electron gas.

relative merit of various values of ϵ_∞ has been given elsewhere.^{1,5} The experimental values of ϵ_1 agree qualitatively with the Drude model for concentrations of 8 MPM and greater. However, the experimental values of ϵ_2 are all higher than the Drude value in this concentration range.

Table I contains values of several parameters related to the plasma resonance: $\hbar\omega_P$, $\hbar\omega_{TT}$, and $\hbar\omega_{ELF}$, where $\hbar\omega_P$ is the free-electron plasma energy derived from density measurements only, $\hbar\omega_{TT}$ is the energy at which $\epsilon_1 = 0$, and $\hbar\omega_{ELF}$ is the energy at which the peak in $\omega\epsilon_2(\epsilon_1^2 + \epsilon_2^2)^{-1}$ occurs. According to the Drude theory, ω_{TT} and ω_{ELF} are given by¹⁰

$$\omega_{TT} = (\omega_P^2 - 1/\tau^2)^{1/2}, \quad (4a)$$

$$\omega_{ELF} = (\omega_P^2 - 1/4\tau^2)^{1/2}. \quad (4b)$$

Values of $\hbar\omega_{TT}$ and $\hbar\omega_{ELF}$ calculated from these formulas using either optical (i. e., α and τ_{opt}) or dc parameters are quantitatively inconsistent with the observations of Figs. 1-3, through the

qualitative order $\omega_P > \omega_{ELF} > \omega_{TT}$ is obtained above 8 MPM. The curve for the observed plasma resonance $\hbar\omega_{ELF}$ is compared to the curve for the free-electron plasma energy $\hbar\omega_P$ in Fig. 4. For concentrations below 8 MPM, the absorption band of the solvated electron shifts the plasma resonance, $\hbar\omega_{ELF}$ away from the absorption band itself (near 0.7 eV) and to energies higher than $\hbar\omega_P$. Hence, the effects of the solvated electron are observed in solutions of concentrations less than 8 MPM. A similar result was observed by Nasby¹¹ in his Hall-effect studies of Li-NH₃ solutions.

Progressively larger deviations from the Drude model are also observed in Figs. 1 and 2 for solutions of concentration less than 8 MPM. The 2-MPM data is, in fact, strongly indicative of the solvated-electron behavior familiar in the dilute solutions.⁴ We find an absorption band near 0.7 eV. Jolly observed the absorption peak of the solvated electron to shift downward from 0.8 eV as the concentration was increased. Koehler¹² found an absorption band in 1 MPM K-NH₃ solutions at approximately 0.72 eV. Therefore, any analysis

TABLE I. Optical parameters of concentrated sodium-ammonia solutions.^a

Concentration (MPM)	14	11	10	8	6	5
α	0.46	0.46	0.45	0.44	0.53	b
$\hbar\omega_P$ (eV)	1.97	1.79	1.72	1.55	1.35	1.25
$\hbar\omega_{ELF}$ (eV)	1.81	1.69	1.60	1.50	1.45	1.32
$\hbar\omega_{TT}$ (eV)	1.80	1.59	1.55	1.37	1.30	1.12
$\langle\tau_{opt}\rangle/\tau_{dc}$	0.45	0.46	0.47	0.48	0.71	0.55
E_F (eV)	0.73	0.64	0.60	0.53	0.44	0.39

^aParameters taken from Ref. 8.

^bELF was too broad for accurate integration.

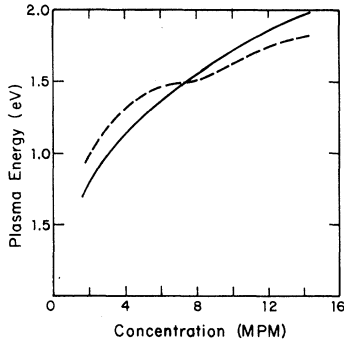


FIG. 4. Parameters associated with plasma oscillations in Na-NH₃ solutions. The solid line depicts $\hbar\omega_p$ as computed from the density, and the dashed line gives the locus of the peaks in the ELF, as shown in Fig. 3. The crossover near 7 MPM is presumed to result from the presence of solvated electrons at low concentrations and the concomitant displacement of the plasma resonance to higher frequencies (see Ref. 13).

of the optical constants of the 2–8-MPM solutions must include contributions from an absorption band due, probably, to the solvated electron. An attempt was made to reproduce the data in this concentration range by adding terms corresponding to bound electrons to Eqs. (1) and (2) and assuming a single absorption band¹³:

$$\epsilon_1 = 1 - \frac{\omega_p^2 \tau^2 f_0}{(1 + \omega^2 \tau^2) + \omega_p^2 \tau_1^2} + \frac{(\omega_1^2 - \omega^2) f_1}{((\omega_1^2 - \omega^2)^2 \tau_1^2 + \omega^2)}, \quad (5a)$$

$$\epsilon_2 = \frac{\omega_p^2 \tau f_0}{\omega(1 + \omega^2 \tau^2)} + \frac{\omega \tau_1 \omega_p^2 f_1}{((\omega_1^2 - \omega^2)^2 \tau_1^2 + \omega^2)}, \quad (5b)$$

where ω_1 is the (experimentally determined) angular resonance frequency, τ_1 is the relaxation time for the bound electrons (determined from the width of the resonance curve), and f_0 and f_1 are the free-electron and bound-electron oscillator strengths, respectively. They are subject to the sum rule $f_0 + f_1 = 1$. The calculated curves showed the same shape as the experimental curves, but the computed values of the real and imaginary parts of the dielectric constant were too small by a factor of almost 2.

There are several possible explanations of the deviations from the Drude model, noted in solutions of concentration 8–20 MPM. The large values of ϵ_2 observed could be accounted for if τ were arbitrarily taken to be a decreasing function of energy in Eqs. (1) and (2). Such behavior has been observed in Cu, Ag,¹⁴ Li,¹⁵ Au, Al,¹⁶ Na,

and K.¹⁷ In Fig. 5, the optical relaxation time τ_{opt} extracted from the data by use of Eqs. (1) and (2) is seen to decrease. In the investigation of the metals mentioned above,^{14–17} no detailed explanations for the cause of this behavior of the relaxation time were given. Some of the authors did speculate that the frequency-dependent relaxation time could be due to a nearby, known absorption edge, the anomalous skin effect, or electron-electron interactions. However, in the concentrated metal-ammonia solutions, no absorption edge has been observed. Also, the criterion for the normal skin effect, $l/\delta \ll (1 + \omega^2 \tau^2)^{3/4}$, where l and δ are the mean-free path and optical skin depth, respectively, is found to be satisfied at all frequencies studied. Values of $\langle \tau_{opt} \rangle / \tau_{dc}$, where $\langle \tau_{opt} \rangle$ is an average of τ_{opt} over the energy range of 0.65 to 1.6 eV and $\tau_{dc} = m_0 \sigma_{dc} / N_0 e^2$, are shown in Table I.

Ron and Lonke¹⁸ have proposed a model consisting of a plasma composed of a degenerate-electron gas and a classical-ion gas, where the self-consistent electron-electron interaction is taken into account phenomenologically, and the ions are not smeared out, but considered as discrete entities. Using this model, they derive an expression for the optical conductivity which is characterized by

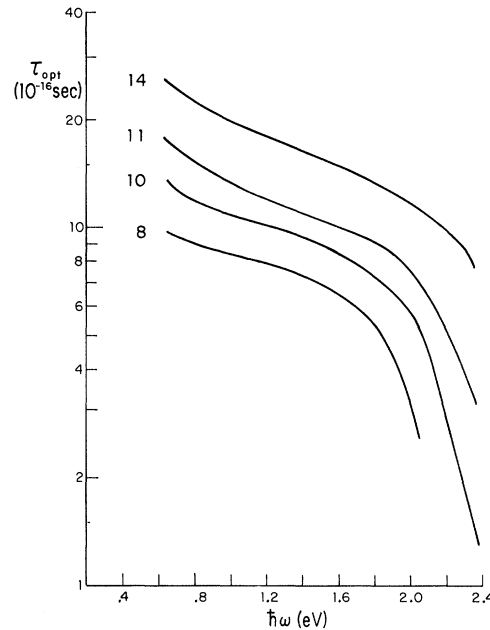


FIG. 5. Optical values of the relaxation time computed from the data of Figs. 1 and 2 using the Drude theory. The dependence of the relaxation time on frequency is presumed to be a consequence of the use of the simple Drude theory when the photon energy is of the order of the Fermi energy, though other causes cannot be excluded (see text).

an effective relaxation time that is frequency-dependent. Applying their results to several metals, they obtain values of ϵ_2 greater than the Drude values and in good agreement with experimental results.¹⁴ The marked deviation from the Drude theory, which they find, occurs for photon energies much less than the Fermi energies of the metals. Although their model has not been widely used, it could provide an explanation for the frequency-dependent relaxation time.

An alternate explanation may lie in the "Amended Drude Theory" of Wilson and Rice,¹⁹ Faber,²⁰ and Baltensperger.²¹ They point out that when photon energies are of the order of, or greater than, the Fermi energy, the usual Drude theory need no longer apply because the electrons do not remain near the Fermi level. Wilson and Rice indicate that ϵ_2 should be greater than the Drude value for monovalent metals in this energy range. In the present work, the Fermi energies of the metal-ammonia solutions studied fall within the range of photon energies, as may be seen from Table I. A calculation¹⁹ of the "amended Drude" value of ϵ_2 has been made using the pseudopotentials and structure factors of Schroeder and Thompson.²² The results for the 14-MPM Na-NH₃ solution show a behavior similar to Wilson and Rice's calculation for Na, but the effect is too small to account for the observations.

There is another possible explanation of some of the data in the concentrated solutions that is quite different from those mentioned above. The observed shifts of the energies $\hbar\omega_{\text{TT}}$ and $\hbar\omega_{\text{ELF}}$, from the free-electron plasma energy (Fig. 4), may result from bound electrons. Wilson¹³ has investigated bound-electron contributions to the shift in the plasma frequency. Since $\omega_{\text{TT}} < \omega_{\text{P}}$ above 8 MPM experimentally, one infers, on the basis of Wilson's theory, the existence of an optical absorption band at a frequency $\omega' > \omega_{\text{P}}$. Burow has observed an ammonia absorption edge⁴ at 2300 Å, and it is possible that this edge could be responsible for the observed shifts in $\hbar\omega_{\text{TT}}$ and $\hbar\omega_{\text{ELF}}$. However, the inclusion of these bound-electron effects in the concentrated solutions invalidates the simple form of the Drude equations (1) and (2), and the comparison of the experimental values with the Drude values mentioned above is no longer meaningful.

Strong arguments can be made in favor of each of the explanations offered, and it is entirely possible that each is applicable simultaneously, or in different concentration or energy ranges. However, it is believed that the ideas of Wilson and Rice, Faber, and Baltensperger are the most pertinent to the present work. The solutions of concentrations greater than 8 MPM agree with the Drude theory only qualitatively, and deviations from this theory are most likely a result of photon energies exceeding the Fermi energies. If the

Drude theory is broadened to include these effects, as in the "amended Drude theory," the need to include bound-electron effects in the concentrated solutions would also be eliminated. A clear choice among these explanations can only be made when data become available in these solutions in the 2000–3000 Å region.

Lithium-Ammonia Solutions

The data from the lithium-ammonia solutions are similar to those reported by Cronenwett¹ and to the Na-NH₃ data, and are not shown. An exceedingly long time was required to obtain data at several temperatures and, therefore, a shorter energy range of 0.65 to 0.92 eV was used in the present work. Figure 6 shows the variation of the energy at which the minimum in ϵ_1 (as seen in Fig. 1 for Na-NH₃ data) occurs with temperature and with concentration. The energy minimum is observed to shift to lower energies as the temperature or concentration is increased. Gold and Jolly⁴ have observed a similar shift in the maximum of the absorbency with concentration and temperature in dilute-alkali metal-ammonia solutions. We infer that solvated-electron effects are present. The further analysis of the data of the concentrated solutions parallels that of the Na-NH₃ solutions, and yields similar results and similar problems.

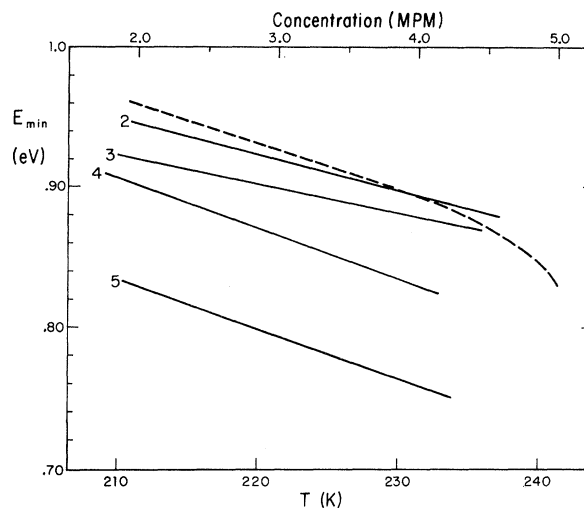


FIG. 6. Shift of the minimum in ϵ_1 (for Li-NH₃ solutions) as a function of temperature and concentration (see Figs. 1 and 8). The solid curves show the temperature dependence for the concentrations shown on the left; the dashed curve shows the concentration dependence at 210 K. This minimum is presumed to be a wing of the dispersion curve associated with the solvated-electron absorption line. The shift to lower energies with increasing concentration is a result of narrowing of the gap between the bound states with increased overlap.

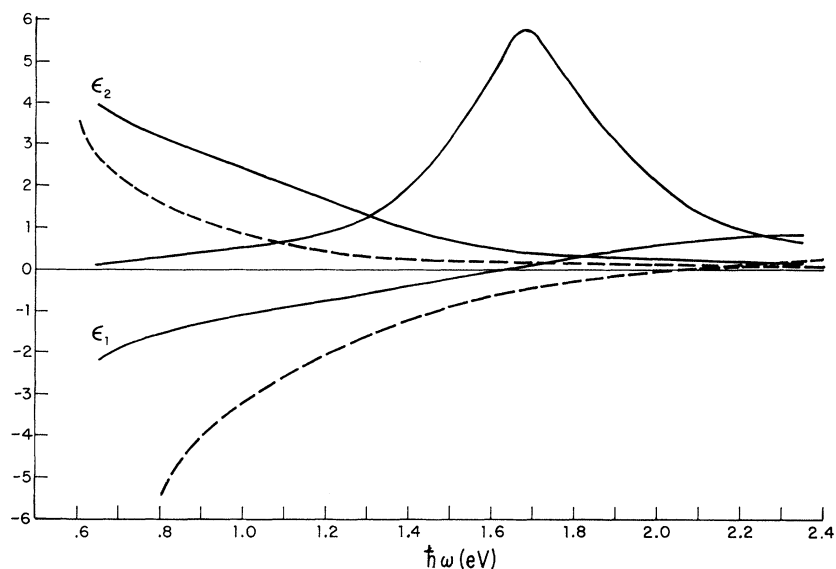


FIG. 7. Real and imaginary parts of the dielectric constant and the ELF for a 6.7 MPM Ca-NH₃ solution at 213 K. The solid lines represent the data and the dashed lines are the result of a Drude-model calculation using dc parameters (see Table II).

Calcium-Ammonia Solutions

Figure 7 shows the real and imaginary parts of the dielectric constant and the energy-loss function for one of two calcium-ammonia solutions studied. The dashed curve indicates a Drude-model calculation, assuming two electrons per atom. The solutions deviate considerably from the Drude model, and the optical relaxation time is found to be frequency-dependent. Since the ion concentration in Ca-NH₃ is down by a factor of 2 from solutions of Li-NH₃ and Na-NH₃ of similar electron concentration, a value of ϵ_∞ other than unity could be highly probable and could certainly affect the frequency dependence of τ_{opt} . Values of α , $\hbar\omega_{\text{P}}$, $\hbar\omega_{\text{ELF}}$, $\hbar\omega_{\text{TT}}$, and $\langle\tau_{\text{opt}}\rangle/\tau_{\text{dc}}$ are shown in Table II. As in the Na-NH₃ solutions, $\hbar\omega_{\text{P}}$, $\hbar\omega_{\text{ELF}}$, and $\hbar\omega_{\text{TT}}$ cannot be accounted for by the simple Drude theory using either dc or optical parameters.

TABLE II. Optical parameters of concentrated calcium-ammonia solutions.^a

Concentration (MPM)	7.5	6.7
α	0.63	0.60
$\hbar\omega_{\text{P}}$ (eV)	2.10	1.99
$\hbar\omega_{\text{ELF}}$ (eV)	1.68	1.57
$\hbar\omega_{\text{TT}}$ (eV)	1.60	1.48
$\langle\tau_{\text{opt}}\rangle/\tau_{\text{dc}}$	0.20	0.21
E_{F} (eV)	0.79	0.74

^aParameters taken from C. W. Tobias and Wa-She Wong, Chem. Abstr. **64**, 1405e (1966); and R. L. Schroeder, J. C. Thompson, and P. L. Oertel, Phys. Rev. **178**, 298 (1969).

Temperature Effects

The effect of temperature on the optical constants was found to be very small for all solutions studied. Figure 8 shows typical variation of the optical constants with temperature for a solution exhibiting nonmetallic characteristics (see also Fig. 6). The temperature coefficients varied with energy and were less than 1%/K. Since this shift is approximately equal to the experimental error, no firm conclusions could be drawn con-

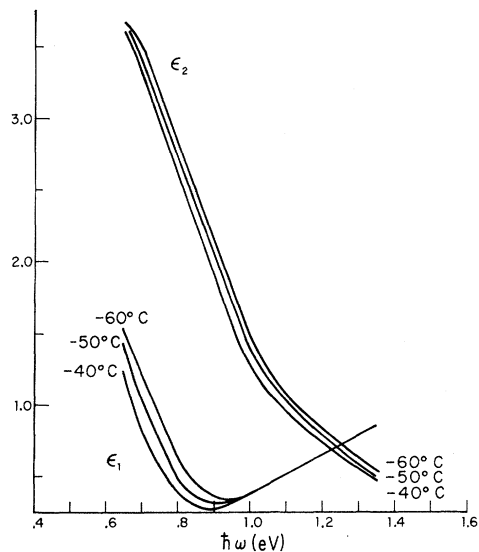


FIG. 8. Temperature dependence of the optical constants of a 3 MPM Li-NH₃ solution. These shifts are consistent with the observed temperature dependence of the solvated-electron absorption line (see Ref. 4).

cerning the magnitude of the temperature coefficients. However, the change of the optical constants with temperature was consistent in all solutions and, therefore, the trend is believed to be real. Temperature effects are larger for low energies, and practically negligible for high energies. The imaginary part of the dielectric constant ϵ_2 is seen to decrease with increasing temperature, and, in the dilute solutions, the peak in ϵ_2 is observed to be washed out, indicating that these solutions become more metallic with increasing temperature.⁵ The temperature shifts observed in these solutions are similar to those seen by Gold and Jolly⁴ in dilute sodium-ammonia solutions.

IV. SUMMARY AND CONCLUSIONS

In solutions of Na-NH₃ of concentrations greater than 8 MPM, ϵ_1 agrees qualitatively with the Drude model, while ϵ_2 is greater than the Drude value, but is still free-electronlike. Evidence of plasma oscillations is found, and the energies $\hbar\omega_{\text{ELF}}$ and $\hbar\omega_{\text{TT}}$ are shifted away from the plasma frequency by an amount that cannot be completely accounted for by the simple Drude theory. Evaluation of the sum rule with $\epsilon_\infty = 1.0$ indicates that $m^* \simeq 2m_0$. The dc conductivity is greater than the optical conductivity for all energies investigated. As the concentration is decreased below 8 MPM, progressively larger deviations from the Drude model are found. The results at 2 and 3 MPM are clearly indicative of bound electrons, and the onset of an absorption band is found at an energy corresponding to the difference between the first two

bound states of the solvated electron. All data taken below 8 MPM show signs of a low-energy absorption band (see Fig. 4).

Dilute solutions of Li-NH₃ were very similar to Na-NH₃ solutions of concentration less than 6 MPM.

The concentrated Ca-NH₃ solutions showed considerable deviation from the Drude model, and evaluation of the sum rule with $\epsilon_\infty = 1.0$ indicates that $m^* \sim 1.6m_0$. These solutions are, therefore, different from solutions of sodium in ammonia and of lithium in ammonia of similar concentration. These differences have not been noted in any previous optical work on calcium-ammonia solutions.²³

The available data cover too narrow an energy range to permit an unambiguous assignment of the source of the small discrepancies between the data and the Drude theory, though the "amended Drude theory" is preferred.

The data, particularly Fig. 4, mark the metal-nonmetal transition as occurring between 2 and 8 MPM. There is clear optical evidence of localized electrons at concentrations just below 8 MPM, and we infer the localized states to be identical with the solvated electron.⁵ The conduction band, in which the free electrons move, is presumed to result from the overlap of the solvated-electron wave functions. The overlap would also presumably broaden the absorption due to localized states and shift it toward lower energies, an effect not seen in the present experiment due to the relatively narrow-wavelength range. No indication was found that the solvated-electron "band" might merge with the band of the solvent, as has been seen in strongly doped semiconductors.²⁴

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²For this paper, the concentration will be expressed either in mole fraction x , where $x = (\text{moles metal})/(\text{moles metal} + \text{moles NH}_3)$, or as mole percent metal (MPM) = 100 x .

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Dynamic Coupling Phenomena in Molecular Excited States. I. General Formulation and Vibronic Coupling H₂

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A general formalism is described for treating diabatic coupling processes in highly excited molecular states. The method treats electronic and nuclear motion quantum mechanically, and uses the adiabatic Born-Oppenheimer states as basis functions. The present paper concentrates on diagnoses of vibronic coupling matrix elements, with Rydberg and continuum states of H₂ as the test cases. The principal contributions come from the excited electron's interactions with the oscillating finite monopole of the ion-molecule core. The electronic factors in the transition amplitudes are definitely dependent on internuclear distance, particularly in the cases of *p* and *d* states. The transition amplitudes accumulate their magnitudes over the full classically allowed range of internuclear distance, especially in the cases of *s* and *p* states. Specific application is made to vibronic coupling perturbations in *pσ* and *pπ* Rydberg states of H₂.

I. INTRODUCTION

The ground electronic states of molecules are, for the most part, well described by wave functions satisfying the Born-Oppenheimer approximation. It is becoming increasingly clear that the same does not hold true for molecular excited states. In small molecules, the coupling of nuclear kinetic and electronic energy is responsible, at least in part, for autoionization and predissociation. The same sort of coupling may give rise to associative ionization and associative detachment or to their inverses of dissociative recombination and dissociative attachment.

Penning ionization, electronic excitation transfer, and vibrational relaxation by electron-molecule collisions can also be induced by transfer of energy between nuclear kinetic and electronic degrees of freedom. Radiationless coupling among bound excited molecular states is associated with broad absorption bands, with anomalously long fluorescence

lifetimes, and with "missing" luminescence; the mechanism of this coupling is generally accepted to be due in major part to breakdown of the Born-Oppenheimer approximation.

It is our purpose here to develop a general theoretical and computational approach to handle a rather large class of phenomena, particularly for small molecules. These include autoionization, predissociation, associative ionization and dissociative recombination, excitation transfer, vibrational relaxation of molecule ions by collision with electrons, and the phenomenon developed most fully in this paper, the vibronic coupling of Rydberg states. We have given a preliminary account of our results for autoionization and predissociation.¹ These topics along with associative ionization and dissociative recombination, will be developed in subsequent work. Our approach, as we shall see, is restricted to relatively low energies, up to a few eV for the collision processes. In the present work, in the background² and preliminary application¹ present-