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# Analysis of Cryodeposit Mixtures

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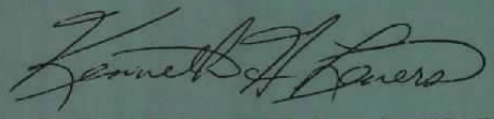

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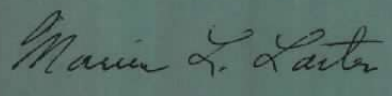

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20 ABSTRACT (Continue on reverse side if necessary and identify by block number)

This work was concerned with the infrared (IR) spectroscopic analysis of the optical properties of cryodeposits and other materials that are important in plume contamination and related studies. The assumption that IR-active molecular band strengths in a material are directly proportional to molecular band species concentrations is incorporated in a method for the calculation of species mole fractions, which is presented along with the results of an analysis of existing AEDC cryodeposit data. The agreement of the calculated mole

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20. ABSTRACT (Continued)

fractions with those obtained from chemical analysis was within 15 percent for binary component cryodeposits, but much worse for multicomponent cryodeposits. During the search for an explanation of the discrepancies, it was found that the accuracies of the densities of the cryodeposits were as crucial as those of the band strengths, and that the above assumption must be modified, in a yet unknown manner, for materials where there is a large degree of hydrogen bonding. Also, it was noted that in mole fraction determinations the use of absorption index values alone is limited to materials having at most one IR-inactive molecular species. However, the identity of IR-inactive species, which must be known in the calculation, must be available from techniques other than IR spectroscopy. A method using molar refractivities for analyzing materials with two or more IR-inactive species is outlined.

Kramers-Kronig and subtractive Kramers-Kronig computer programs were written for the analysis of non-normal reflectance data from a single interface, for the calculation of absorption index values from an n-spectrum, and for the finding of the optical constants of a single film thickness on a thick substrate using transmittance measurements. A Kramers-Kronig program for obtaining the optical constants of a single film thickness also seems possible. The need for more optical data of substrate materials at cryogenic temperatures is stressed.

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## PREFACE

The research reported herein was conducted by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC). The analysis was performed by Westminster College, Fulton, Missouri, under subcontracts No. 78-22-VKF and 79-18-VKF for ARO, Inc. (a Sverdrup Corporation Company), operating contractor of AEDC, AFSC, Arnold Air Force Station, Tennessee. The work covered the period from October 1, 1977 to September 1, 1979 and was done under ARO Project Numbers V32S-R1A, V32K-13A, and P32K-13A. Dr. H. E. Scott, Directorate of Technology, was the Air Force project manager. The manuscript was submitted for publication on September 25, 1979.

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## TABLE



## APPENDIX

# 1.0 INTRODUCTION

Contamination of spacecraft and satellite surfaces and components by exhaust products from spacecraft thrusters, outgassing products, and other contamination sources are of considerable concern to the spacecraft designers. This concern is attributed to the development of more sophisticated spacecraft systems designed to perform multiple, noninterfering missions for longer periods of time in space. Contamination and subsequent degradation of sensitive optical components can compromise mission objectives. It is for these reasons that effects of condensed gases on optical surfaces has received widespread interest.

Much of the effort in the past studies of the radiative properties of cryodeposit-coated surfaces and materials has been experimental in nature. The quantity of experimental data recently generated for condensed gases has necessarily emphasized the experimental portion of this subject. The theoretical and analytical side of this study, although initiated earlier for determining refractive and absorption indices (n's and k's) from transmission measurements, has been lagging. Further extension, therefore, of various mathematical models was deemed plausible for determining n's and k's of deposited films and of optical substrate materials using both transmission and reflectance measurements. In addition, from the transmission measurements of the pure, condensed gases and of mixtures of gases, efforts have been undertaken to try and determine the mole fractions of various species of gases condensed in a matrix. These fractions, determined by relative absorption band strengths, were compared to mole fraction values determined experimentally.

The overall objectives of this work are to provide improved analytical methods for determining mole fractions of condensed rocket exhaust gases and their optical properties (n,k) from spectroscopic transmittance or reflectance data. To accomplish these overall objectives, the following specific areas were investigated:

1. Determination of the mole fractions of cryodeposit constituents.
2. Determination of the optical indices n and k of a medium from non-normal reflectance measurements of a single interface of the medium with either air or a vacuum.
3. Calculation of the absorption index, k, of a material from known values of the refractive index, n.
4. Obtaining the optical indices of a thin film from transmittance measurements of the film on a thick substrate.

5. Finding the optical indices of a thin film from reflectance measurements of the film on a thick substrate.

6. Measurement of the optical indices of substrates at cryogenic temperatures.

7. The use of the molar refractivity of materials in mole fraction determinations.

Progress in accomplishing these items is described in the following sections of this report.

## 2.0 MOLE FRACTIONS OF MOLECULAR SPECIES IN HOMOGENEOUS CRYODEPOSITS

### 2.1 BASIC THEORY

Several spectroscopic methods for finding concentrations of molecular species in cryodeposits were examined by one of the authors, K. F. Palmer, during the 1976 USAF-ASEE Summer Faculty Research Program at AEDC. The most promising method is based on the assumption that the number density and the molar concentration of the $i^{th}$ molecular species, $c_i$, is directly proportional to the band integral if species i is infrared (IR)-active (Ref. 1):

$$\int_{\text{Band } j} k_i(\nu)\, d\nu, \text{ i.e., } \quad c_i \propto \int_{\text{Band } j} k_i(\nu)\, d\nu \tag{1}$$

Here, $c_i$ has the dimensions of moles per unit volume and $k_i(\nu)$ is the contribution of species i to the absorption index of the homogeneous medium at the wavenumbers, $\nu$, surrounding the $j^{th}$ absorption band characteristic of molecular species i. This assumption implies that changes in the intermolecular forces should not affect the integral of $k_i$ over the absorption region even though the shape of the absorption index curve may be altered. It is known that the formation and breaking of hydrogen bonds can cause anomalous intensity variations in intramolecular absorption bands (Ref. 2). Thus, especially for $H_2O$ molecules, Eq. (1) may need modification in some instances (see Section 2.2).

A second assumption is that for $k(\nu)$ of a given homogeneous material,

$$k(\nu) = \sum_{\ell=1}^{N} k_\ell(\nu) \tag{2}$$

when there are N molecular species in the material (Ref. 2). Therefore,

$$k_i(\nu) = k(\nu) - \sum_{\substack{\ell=1 \\ \ell \neq i}}^{N} k_\ell(\nu) \tag{3}$$

where the summing term does not include the $\ell = i$ term and represents the effects of "background" absorption on the absorption attributed to molecular species i. In practice, the determination of the background is somewhat ambiguous, and variations in background values can have noticeable effects upon the results (see Section 2.2).

The molar concentration of any molecular species i, $c_i$, in a sample can be calculated if the ratio $R_i = c_i/c_{si}$ is known. The "standard" molar concentration, $c_{si}$, is the previously measured concentration of species i in a "standard" material that usually contains only the $i^{th}$ molecular species and is at the same temperature as the sample. For IR-active molecular species Eq. (1) gives

$$R_i \equiv c_i/c_{si} = \int_{\text{Band } i} k_i(\nu)\, d\nu \Big/ \int_{\text{Band } i} k_{si}(\nu)\, d\nu \tag{4}$$

where $k_i(\nu)$ is given by Eq. (3) and $k_{si}(\nu)$ is the analogous quantity for the standard material. Note that the band shapes in the $k_i(\nu)$ and $k_{si}(\nu)$ curves may not be the same and the domains of integration may not be identical.

Once the molar concentrations of the IR-active and inactive molecular species in a material are known, the mole fraction of species i, $f_i$, can be calculated from

$$f_i = c_i \Big/ \sum_{\ell=1}^{N} c_\ell \tag{5}$$

where N is the total number of IR-active and inactive species. Of course,

$$\sum_{i=1}^{N} f_i = 1 \tag{6}$$

and if all but one of the molar concentrations are known, the unknown molar concentration, say, $f_N$ where species N is IR-inactive, could be found from

$$f_N = 1 - \sum_{i=1}^{N-1} f_i \tag{7}$$

The molar concentrations of species in materials are related to the densities of the materials. If the standard material for species i contains only species i molecules, the density of the standard material, $\varrho_{si}$, is

$$\rho_{si} = c_{si} M_i \tag{8}$$

where $M_i$ is the molecular mass of species i with the dimensions of mass/mole. If Eq. (8) is used in the first equation of Eq. (4), the molar concentration of species i in another material can be found from

$$c_i = \rho_{si} R_i / M_i \tag{9}$$

However, $R_i$ can be found from the band integrals [second equation of Eq. (4)] only for IR-active species; $R_i$ for IR-inactive species must be obtained by other means such as Raman spectroscopy, or the molar refractivities (see Section 8.0).

If only IR spectra are available, the mole fractions of the molecular constituents in a given material can be found if at most one IR-inactive species is present, whose identity is known by other methods, such as Raman spectroscopy. In the case that no IR-inactive species is in the material, substitution of Eq. (9) into Eq. (5) gives the mole fraction of species i as

$$f_i = \left( \rho_{si} R_i / M_i \right) \Bigg/ \sum_{\ell=1}^{N} \rho_{s\ell} R_\ell / M_\ell \tag{10}$$

The Appendix shows that for small relative errors $\Delta R_i / R_i$ and $\Delta \varrho_{s\ell} / \varrho_{s\ell}$ in $R_\ell$ and $\varrho_{s\ell}$, respectively, the relative error in $f_i$ is approximately

$$\Delta f_i/f_i = \Delta R_i/R_i - \Delta\rho_{si}/\rho_{si} - \sum_{\ell=1}^{N} f_\ell\left(\Delta R_\ell/R_\ell + \Delta\rho_{s\ell}/\rho_{s\ell}\right) \tag{11}$$

Note in Eq. (11) that if the relative errors in the densities, $\varrho_{s\ell}$, are comparable to those of the concentration ratios, $R_\ell$, the influence of the density errors and the influence of the ratio errors upon the calculated mole fraction of a species are also comparable.

If molecular species N is the only IR-inactive species present in some material, Eq. (5) can be written

$$f_i = c_i/\left(\sum_{\ell=1}^{N-1} c_\ell + c_N\right) \tag{12}$$

or

$$f_i = \left(\rho_{si} R_i/M_i\right)\Big/\left(\sum_{\ell=1}^{N-1} \rho_{s\ell} R_\ell/M_\ell + c_N\right)$$

when Eq. (9) is used for the molar concentration of the IR-active species. The molar concentration of the IR-inactive species N, $c_N$, cannot be found from Eq. (9) because $R_N$ is unknown. However, $R_N$ may be calculated from the average density, $\varrho$, of the sample material:

$$\rho = \sum_{\ell=1}^{N} c_\ell M_\ell \equiv \sum_{\ell=1}^{N-1} c_\ell M_\ell + c_N M_N$$

Here, $c_\ell M_\ell = C_{s\ell} R_\ell M_\ell = \varrho_{s\ell} R_\ell$, from Eq. (8). Thus, $c_N = (\varrho - \sum_{\ell=1}^{N-1} \varrho_{s\ell} R_\ell)/M_N$ and Eq. (12) is

$$f_i = \left(\rho_{si} R_i/M_i\right)\Big/\left(\sum_{\ell=1}^{N-1} \rho_{s\ell} R_\ell \left(\frac{1}{M_\ell} - \frac{1}{M_N}\right) + \rho/M_N\right) \tag{13}$$

The relative error of $f_i$ is approximately

$$\Delta f_i/f_i = \Delta R_i/R_i + \Delta\rho_{si}/\rho_{si} - \Delta\rho/\rho - \sum_{\ell=1}^{N-1} f_\ell\,(M_\ell/M_N - 1)(\Delta R_\ell/R_\ell + \Delta\rho_{s\ell}/\rho_{s\ell} - \Delta\rho/\rho) \tag{14}$$

when the errors in $R_\ell$, $\varrho_{s\ell}$, and $\varrho$ are small (see the Appendix). Again, the relative errors of the densities can be just as important as the relative errors of the concentration ratios in causing errors in the calculated mole fractions.

In summary, the mole fractions of molecular constituents in a sample material can be found from infrared spectra using either Eq. (10) or (13) if the densities of the sample and the standard materials are known and if the ratio R of the sample molar concentration to the molar concentration of the standard material are measured for all, or all but one, constituent molecular species. For IR-active species the concentration ratios R are assumed identical to ratios of the appropriate band integrals (Ref. 1). Also, accurate determination of the mole fractions of species depends as much on the accuracy of the density values as on the accuracy of the band integral ratio values.

## 2.2 EXPERIMENTAL RESULTS

Table 1 contains the results of the application of Eqs. (10) and (13) to AEDC cryodeposit data previously analyzed by W. B. Newbolt during the 1977 USAF-ASEE Summer Faculty Research Program at AEDC. In the two columns next to the last one the mole fractions calculated in the present analysis are compared to the mole fractions found from chemical analysis of the residual gas mixture used to form the cryodeposits. Note that the calculated mole fractions are not identical to the ratios of the band integrals. In the last column the mole fractions calculated by Eq. (10) or (13) from the band integral ratios of Newbolt are given. In most cases Newbolt's choice of band integrals differed from those in the table, and there were no allowances made for any background absorption.

The agreement of the present mole fraction values with those from chemical analysis is within 15 percent for the two-component cryodeposits, but is much worse for the Plume I film composed of a simulated plume mixture of gases. In particular, the concentration of water ($H_2O$) molecules was calculated to be much less than was found chemically. This discrepancy is most likely due to the anomalous behavior of $H_2O$ absorptions caused by hydrogen bonding, an effect that depends, in part, on the concentration of $H_2O$ molecules. For pure $H_2O$, the absorption band intensities of intramolecular vibrations of condensed phases are approximately an order of magnitude greater than the corresponding vapor phase intensities attributable mainly to the increased hydrogen bonding in the condensed phases (Ref. 2). Although more study on the effects of hydrogen bonding in cryodeposits is necessary, it should be noted that the band integral of the librational band of liquid water, $\nu_{lib}$, is very nearly temperature independent and so, presumably, is nearly independent of the local molecular environment (Ref. 3). It might be possible to use the librational band of $H_2O$ in cryodeposits as a more accurate index of $H_2O$ concentration. To do this the domain of the IR data must be extended down to about 500 $cm^{-1}$; this can only be done by obtaining accurate measurements of the optical properties of the substrate at cryogenic temperatures (see Section 7.0).

In the calculations, a consistent set of cryodeposit densities is used throughout. In all cases, however, better agreement with the mole fraction determined from chemical analysis is possible if slightly different values of the densities are used in each separate calculation. The densities given in Table 1 for the dinitrogen/water mixture ($N_2/H_2O$), carbon monoxide (CO), and Plume I cryodeposits as well as that of pure $N_2$ (which was not used in the calculations) are those found during the original transmission measurements. The density of pure carbon dioxide ($CO_2$) is the value determined by Arnold et al. (Ref. 4), that of $H_2O$ is the mean value of several $H_2O$ cryodeposits measured at AEDC, and the densities of the remaining mixtures represent the mean of the tabulated densities of the standard (pure) cryodeposit of the constituent species, weighted according to their approximate molar concentrations.

Except for those marked by asterisks, the band strengths (integrals) given in Table 1 are found by numerical integration of the data over the indicated wavenumber domains. If the k value at either endpoint of the domain was not zero, a background absorption was computed and subtracted from the integrals to give the tabulated band strength, S.

There is a degree of arbitrariness in choosing the limits of integration and accounting for extraneous absorptions. A "moment" method for finding the baseline and the limits of integration of unblended bands has been shown by Jiang et al. (Ref. 5) to reduce the experimental uncertainties in the computation of band strengths, and it is recommended that the "moment" method be tried and evaluated in future band strength calculations. Blended absorptions were decomposed by a nonlinear least-squares fit of the data to two or more Lorentzian line shapes. For instance, the $\nu_2$ band of $H_2O$ is badly blended by lattice vibration absorptions in the pure $H_2O$ cryodeposit and is blended by other absorptions in the Plume I cryodeposit. Lattice bands also contribute to the absorption of the $1 \leftarrow 0$ band of $^{12}CO$ and, to a lesser extent, the $\nu_3$ band of $^{12}CO_2$ (Ref. 5). For these reasons, absorptions attributable to $^{13}CO$ and $^{13}CO_2$ were used whenever possible, although the much lower band intensities of the $^{13}C$ isotopic species are subject to larger experimental errors. For the Plume I cryodeposit, only the $\nu_3$ band of $^{12}CO$ was sufficiently "clean" of extraneous absorptions so that its band strength could be found by numerical integration of the original data. The other band strengths in the Plume I cryodeposit, and those of the standard cryodeposits, are computed from Lorentzian fits because of the blends cited above. It should be noted that the Lorentzian band strength for the $1 \leftarrow 0$ band of $^{12}CO$ is greater than the band strength found by direct integration, because of the large "wings" of the Lorentzian line shape. This suggests that a Gaussian or Voight profile might better approximate the line shapes of the data.

## 3.0 OPTICAL INDICES OF A MEDIUM FROM NON-NORMAL REFLECTANCE MEASUREMENTS OF A SINGLE INTERFACE

The optical constants $n(\nu)$ and $k(\nu)$ at wavenumber $\nu$ of a material can be obtained from reflection measurements of a light beam at the interface of the material with a vacuum or air. Kramers-Kronig (KK) techniques allow both n and k to be found from the reflectance of a beam of electromagnetic radiation at the interface using measurements at just one angle of incidence. Of course the material must have dimensions and a geometry that will not allow extraneous radiation to enter the spectrometer; precautions are especially necessary at wavenumbers where the material is nearly transparent. For non-normal incidence the components of the electric and magnetic fields parallel and perpendicular to the plane of incidence have reflectances that become measurably different at beam incident angles greater than about 10 deg (Ref. 6).

The complex reflectivity if $\hat{r}(\nu) = [R(\nu)]^{1/2} \exp [i\phi(\nu)]$, where the circumflex denotes complex quantities, i is $(-1)^{1/2}$, R is the measured reflectance, and $\phi$ is the phase shift of the beam upon reflection. Two KK dispersion relations between R and $\phi$ can be written in which one of the quantities is evaluated at a given wavenumber in terms of an integral of the other quantity over all wavenumber space. In our case the reflectance, R, is measured experimentally and the phase shift, $\phi$, can be found from

$$\phi(\nu) = \frac{2\nu}{\pi} P \int_0^\infty \frac{\ell n\,[R(\nu')]^{1/2}\, d\nu'}{\nu^2 - \nu'^2} \qquad (15)$$

where P denotes the Cauchy principle value. The optical constants are obtained from

$$n = \left\{ \left[ \left(Q^2 - S^2 + \sin^2\theta\right) - \left[ \left(Q^2 - S^2 + \sin^2\theta\right)^2 - 4Q^2 S^2 \right]^{1/2} \right] \Big/ 2 \right\}^{1/2}$$

and

$$k = SQ/n$$

where

$$Q = (1 - R)\cos\theta \,/\, (1 + R - 2R^{1/2}\cos\phi)$$

and

$$S = 2R^{1/2}\sin\phi\cos\theta \,/\, (1 + R - 2R^{1/2}\cos\phi)$$

for a beam angle of incidence $\theta$. Note, however, that for non-normal incident angles, the reflectances of different polarization components of the beam will vary. It is important that

the reflectance of only one polarization component be used in these equations when $\theta >>$ 10 deg.

The finite range of measured reflectance data means that extrapolations of R-values to $\nu = 0$ and to $\nu = \infty$ are necessary. In the present case the R-values are assumed to be constant outside the measured data domain with $R(\nu) = R(\nu_L)$ for $0 < \nu < \nu_L$, and $R(\nu) = R(\nu_H)$ for $\nu > \nu_H$.

The errors introduced by various extrapolations of reflectance data and other experimental uncertainties have been discussed by Bowlden and Wilmshurst (Ref. 7) and Hale et al. (Ref. 8). The former authors have studied the effects of neglecting all contributions to the integral of Eq. (5) outside the domain of the data. This is equivalent to assuming that R is 1 when $0 < \nu < \nu_L$ or $\nu > \nu_H$. Using comparisons to theoretical dispersion curves, they show that the k-values from the KK analysis of an abosrption band are within a few percent of the theoretical values as long as the data limits are sufficiently far from the band center, say, greater than 10 band half-widths. When they varied the limits of integration, which is analogous to changing the extrapolation conditions of actual reflectance data, the most noticeable effect they found was some (asymmetric) distortion of the band shape, a result in accord with the authors' experience with liquids. This effect was minimized for a given band centered at $\nu_0$ when the limits of integration were chosen so that $\nu_0/\nu_L \approx \nu_H/\nu_0$. Under these conditions the errors caused by neglecting the high and low wavenumber regions cancel almost completely, except for wavenumbers within a small region about the band center. There the errors are additive but very small. Thus, it appears that the k values determined by the KK method are relatively insensitive to the details of extrapolations used outside the data domain, and it is the authors' experience that the n values determined by the KK method are even less sensitive.

Hale et al. (Ref. 8) have shown that when the reflectance is analyzed by KK techniques, the effect of random relative errors in the IR reflectance values of liquid water cause approximately the same values of relative error in all n values and in the k values within an absorption. The random relative errors for k values become large at wavenumbers far from absorptions. These results should apply to work on other dielectrics because of similar reflectance and error values.

The influence of systematic errors in the reflectance upon the optical constants from KK analysis is felt to be minimal. Consider the special case in which all "true" reflectance values, R, are changed by some systematic error to $R' = \beta R$, where $\beta$ is a constant. Now, Eq. (15) when integrated by parts is

$$\phi(\nu) = \frac{1}{\pi} P \int_{\ln\sqrt{R(0)}}^{\ln\sqrt{R(\infty)}} \ln \left| \frac{\nu - \nu'}{\nu + \nu'} \right| d\left(\ln\sqrt{R}\right)$$

If R' were used in the integral instead of R, the differential would become $d(\ln\sqrt{R'}) = d(\ln\sqrt{\beta R}) = d(\ln\sqrt{\beta}) + d(\ln\sqrt{R}) = d(\ln\sqrt{R})$ are the phase shift, $\phi$, would remain unchanged from the "true" value. In other instances of systematic error where $\beta$ is a slowly varying function of wavenumber compared to $\ln\sqrt{R}$ the changes in $\phi$ would be very small.

Ahrenkiel (Ref. 9) has shown that subtractive Kramers-Kronig (SKK) dispersion relations reduce the errors in the optical constants associated with extrapolations. Essentially SKK values of the optical constants are made relative to a known value of that constant at a wavenumber $\nu_o$, which is within the wavenumber domain of the data. For reflectance measurements from a single air-material or vacuum-material interface, the appropriate SKK relation for the phase shift is

$$\phi(\nu) = \nu \left\{ \frac{\phi(\nu_o)}{\nu_o} + \frac{\nu_o^2 - \nu^2}{\pi} P \int_0^\infty \frac{\ln R(\nu')\, d\nu'}{(\nu^2 - \nu'^2)(\nu_o^2 - \nu'^2)} \right\} \tag{16}$$

Here, R is the reflectance of a single component of polarization that is usually the component perpendicular to the plane of incidence if the angle of incidence, $\theta$, is not zero. The optical constants can be found from the above relations.

Computer programs "KKANR" and "SKKR" (written by K. F. Palmer) incorporate Eqs. (15) and (16), respectively, for KK and SKK analysis of reflectance data. The input data to the programs can be arbitrarily spaced according to wavenumber. The integration is done numerically by Simpson's rule except near the singular points and where three consecutive data points are not equally spaced in wavenumber. In these cases the numerator of the integrand is approximated by a quadratic function fitted to three consecutive data points, and the integration is computed analytically.

Both "KKANR" and "SKKR" have been used to analyze the ice reflectance data of Schaaf (Ref. 10). The agreement between the two programs for the optical constants is excellent if some care is exercised is choosing $\nu_o$ for the latter program, such as using a $\nu_o$ value that is far from any absorptions. Also, the values determined by these programs for all n values and those k values surrounding molecular absorptions are within one percent of the values given by the KK analysis of Schaaf. However, the k values far from absorptions are sometimes substantially different from those of Schaaf and may even be negative. Part of the discrepancy may be due to the difference in algorithms for obtaining the contribution to the integrals about a singular point. The authors feel the present algorithm is more accurate, however, and suggest further investigation of the matter.

## 4.0 ABSORPTION INDEX k($\nu$) FOUND BY THE KRAMERS-KRONIG ANALYSIS OF n($\nu$)

Kramers-Kronig dispersion relations can be written for the real and imaginary components, or the modulus and phase angle, of many well-behaved complex functions. In particular, the KK equations for n and k (the real and imaginary components of the complex refractive index n) can be used to find k if n is known over a wide wavenumber region, and vice-versa. The relations can also be used to check the internal consistency of optical data.

The KK relations for n and k are

$$n(\nu) = n(\infty) + \frac{2}{\pi} P \int_0^\infty \frac{\nu' k(\nu') d\nu'}{\nu'^2 - \nu^2} \tag{17}$$

and

$$k(\nu) = \frac{2\nu}{\pi} P \int_0^\infty \frac{n(\nu') d\nu'}{\nu^2 - \nu'^2} \tag{18}$$

where n($\infty$) is the contribution to the index of refraction as $\nu$ goes to infinity (Ref. 4). The corresponding SKK relations are easily shown to be

$$n(\nu) = n(\nu_o) + \frac{2(\nu^2 - \nu_o^2)}{\pi} P \int_0^\infty \frac{\nu' k(\nu') d\nu'}{(\nu^2 - \nu'^2)(\nu_o^2 - \nu'^2)} \tag{19}$$

and

$$k(\nu) = \nu \left[ \frac{k(\nu_o)}{\nu_o} + \frac{2(\nu_o^2 - \nu^2)}{\pi} P \int_0^\infty \frac{n(\nu') d\nu'}{(\nu^2 - \nu'^2)(\nu_o^2 - \nu'^2)} \right] \tag{20}$$

where n($\nu_o$) and k($\nu_o$) are found at $\nu = \nu_o$ by a separate measurement. A computer program utilizing Eq. (19) is presently in use at AEDC (Ref. 11). Computer programs "KKN2K" and "SKKN2K" have been written (by K. F. Palmer) to calculate k from known n values using Eqs. (18) and (20), respectively. Outside the data domain $\nu_L \le \nu \le \nu_H$ the values of k are assumed to be k($\nu_H$) for the $\nu > \nu_H$ and k($\nu_L$) for $0 < \nu < \nu_L$.

Program "SKKK2N" has also been written (by K. F. Palmer) to obtain n values from k values. As a check on the internal consistency of programs "SKKK2N" and "SKKN2K", they were run in sequence. The AEDC-observed values of k($\nu$) in the range from 700 $cm^{-1}$ to 3,700 $cm^{-1}$ (including the finely spaced points in the absorption bands) for $CO_2$ were used in SKKK2N to obtain the n($\nu$) spectrum. These n($\nu$) values were then used as input for the SKKN2K program, yielding a k($\nu$) spectrum (k-calculated) that could then be compared with the original AEDC values. The differences between the original k-observed and k-calculated values were substantial—consistently less than 0.2 except at the peak of the $\nu_3$ band of $CO_2$, where the difference was approximately 0.3, and near the lower end of the observed spectrum (710 to 1030 $cm^{-1}$) where the differrences were as much as 0.565.

There are several plausible explanations for these discrepancies, including coding errors in the computer programs, numerical/analytical errors (such as formula derivations), and inaccurate data. It is encouraging that the error, (k-observed) - (k-calculated), appears to be quite regular. Indeed, the values of k-observed and k-calculated, as well as their difference, were plotted and compared. The $\nu_3$ band of $CO_2$ in particular had the same shape and location, but appeared to be shifted downward by approximately 0.2. This leads us to believe that there may be a programming or numerical/analytical error, and thus further investigation of the consistency of the SKK relations, and the corresponding programs, will begin here.

## 5.0 OPTICAL CONSTANTS OF A THIN FILM ON A THICK SUBSTRATE FROM TRANSMITTANCE MEASUREMENTS

At present at AEDC, the optical constants of thin films deposited on thick substrates are determined by a separate calculation at each wavenumber using the dependence of the transmittance of a beam through the film and substrate upon the thickness of the film. A lamellar model of the film and substrate (Ref. 12), which includes interference effects, is treated by a nonlinear least-squares procedure to extract the optical constants at a given wavenumber. One of the underlying assumptions of this method is that the optical properties of the film do not change with thickness.

Meada et al. (Ref. 13) have shown that KK relationships can be written for the modulus and phase angle of the complex transmission coefficient, t, of a single film thickness on a substrate, where $t(\nu) = T(\nu)^{1/2} e^{i\phi(\nu)}$ and $T(\nu)$ is the measured transmittance at wavenumber $\nu$. The KK relation of interest is

$$\phi(\nu) = \frac{\nu}{\pi} P \int_0^\infty \frac{\ell n\, T(\nu')\, d\nu'}{\nu^2 - \nu'^2} + 2\pi\nu d \qquad (21)$$

where d is the film thickness. The corresponding SKK equation is

$$\phi(\nu) = \nu\left\{\frac{\phi(\nu_o)}{\nu_o} + \frac{\nu_o^2 - \nu^2}{\pi} P\int_o^\infty \frac{\ell n\, T(\nu')\, d\nu'}{(\nu^2 - \nu'^2)(\nu_o^2 - \nu'^2)}\right\} \quad (22)$$

$\phi(\nu_o)$ being the phase angle at $\nu_o$ determined from a separate measurement at that film thickness. Either equation can be used to evaluate $\phi$ of a single thickness of film, and both optical constants n and k can be found for that thickness by a nonlinear interpolation of the complicated functions relating n, k, T, and $\phi$ (Ref. 13).

A computer program, which analyzes transmittance data at a single film thickness according to Eq. (22), was applied to AEDC data of a CO cryodeposit with a film thickness near the midrange of the observed thicknesses. In most instances this SKK program was successful in converging to the same n and k values found by using the dependence of the transmittance upon film thickness. Sometimes, however, especially near molecular absorptions, more than one physically reasonable pair of n and k values will give identical values of T and $\phi$, and the two methods will not agree. At present potential algorithms for finding the "best" values of n and k are being tested. It may, for example, be necessary to analyze data from two (or more) film thicknesses simultaneously, so that by comparison of the possible solutions for both thicknesses, the unwanted solutions might be eliminated.

## 6.0 OPTICAL CONSTANTS FROM REFLECTANCE MEASUREMENTS OF A THIN FILM ON A SUBSTRATE

Radiation reflected from a thin-film cryodeposit on a metal substrate has been analyzed by using the dependence of the reflectance upon film thickness at a given wavenumber (Ref. 4). As in the analysis of transmittance data, a lamellar model of the film and the substrate was used, and it was assumed that the optical constants of the film are independent of film thickness.

From the results given in Section 5.0, it seems feasible that usable KK relations exist for the modulus and phase angle of the complex reflection coefficient $r(\nu) = R(\nu)^{1/2}\, e^{i\phi(\nu)}$, where $R(\nu)$ is the measured absolute reflectance (or the reflectance relative to a bare substrate) of a single film thickness. The main criterion for determining the usefulness of a KK relation is that the value of the desired optical property be finite and determinate as the wavenumber approaches zero or infinity. At present the value of $\phi(\infty)$ of $\hat{r}$ is not known, although a preliminary investigation indicates the value is very likely zero. If a suitable $\phi(\infty)$ value is found in future work, computer programs similar to the one being tested (Section 5.0) can result, giving a KK method of obtaining the optical constants n and k.

## 7.0 OPTICAL CONSTANTS OF SUBSTRATE MATERIALS AT CRYOGENIC TEMPERATURES

In the lamellar model of a thin film on a substrate, the optical constants of the film can be found if those of the substrate are known (see Sections 5.0 and 6.0). There are, however, few reliable data on the cryogenic optical properties of substrate materials in the literature, and "in-house" measurements must be made. At present, measurements of the optical constants of germanium at 20 and 80 K have been made in the range from 700 to 3,700 $cm^{-1}$ (Ref. 12). Section 2.0 describes the need to observe molecular absorptions of cryodeposits beyond the high and low limits of this wavenumber region. This can be accomplished if the range of germanium measurements is expanded and/or data are obtained for other substrate materials.

The analysis of the transmittance or reflectance of two substrate thicknesses is the most direct way of determining the optical properties of the substrate, but this analysis may be expensive or otherwise inconvenient. A KK analysis of a single thick film of substrate material is not possible because of the loss of phase information. Another alternative for finding substrate optical properties is the analysis of reflectance measurements from a single interface of substrate material through an appropriate KK, or SKK, relation (see Section 3.0). However, shaping the sample into a geometry such as a light horn (Ref. 14), that is, suitable for the elimination of stray reflections, may not be practical for some materials, especially for transparent wavenumber regions.

## 8.0 MOLAR REFRACTIVITY OF MATERIALS - DETERMINATION OF MOLECULAR SPECIES CONCENTRATIONS IN MATERIALS CONTAINING MORE THAN ONE INFRARED-INACTIVE SPECIES

The molar refractivity, A, of a material containing a single nonpolar molecular species is, at wavenumbers far from absorptions,

$$A \equiv \frac{4\pi}{3} N_A \alpha = \frac{N_A}{N} \frac{n^2 - 1}{n^2 + 2} = \frac{M}{\rho} \frac{n^2 - 1}{n^2 + 2} \tag{23}$$

where $N_A$ is Avogadro's number, $\alpha$ is the molecular polarizability, N is the number density, M is the molecular mass per mole, and $\varrho$ is the mass density of the material (Ref. 6). If there are N chemically inactive molecular species in a homogeneous mixture, with density $\varrho$ and refractive index n, the molar refractivity of the mixture is approximately

$$A = \sum_{i=1}^{N} c_i A_i \Big/ \sum_{i=1}^{N} c_i$$

where $c_i$ is the molar concentration (moles per unit volume) of species i in the mixture and $A_i$ is its molar refractivity. Equation (23) and the above equation can be combined to show

$$\sum_{i=1}^{N} \frac{c_i M_i}{\rho} \frac{n^2 - 1}{n^2 + 2} = \sum_{i=1}^{N} \frac{c_i M_i}{\rho_{si}} \frac{n_{si}^2 - 1}{n_{si}^2 - 2} \tag{24}$$

where $M_i$ is the molecular mass per mole of species i, $\rho_{si}$ is the known density, and $n_{si}$ is the known refractive index of the "standard" material for species i.

In principle, the concentrations $c_i$ could be determined from the values of the densities and indices of refraction measured at least N different wavenumbers, allowing the calculation of the mole fractions by Eq. (5) of Section 2.0. However, for wavenumbers far from absorptions the indices ordinarily do not change noticeably with wavenumber, and a numerical solution of Eq. (24) may be difficult, or impossible, to achieve for a material with many molecular species. It appears feasible, though, that an interative method incorporating Eqs. (4) and (24) for the IR-active and inactive species, respectively, could be devised so that the molecular concentrations can be obtained for materials containing more than one IR-inactive molecular species. Of course, as for the materials containing just one IR-inactive species (Section 2.0), the identities of the inactive species must be found from techniques other than IR spectroscopy, e.g., Raman spectroscopy. A matter of further study will be to determine the effect of applying Eq. (24) to materials containing strongly polar molecules such as $H_2O$.

## 9.0 SUMMARY

The overall objective of this work was to provide improved analytical methods for determining mole fractions of condensed rocket exhaust gases and their optical properties from spectroscopic transmittance and reflectance data. Seven specific areas (see Section 1.0) were investigated to further progress toward the overall goal, and the results may be summarized as follows.

1. The investigation made for determining molar concentrations indicated that mole fractions can be found from infrared spectra if the densities of the sample and standard materials are known and if the ratio R of the sample molar concentration to the molar concentration of the standard material is measured for all, or all but one, constituent molecular species. It was also shown that accurate determination of the mole fractions of species depends as much on the accuracy of the density values as on the accuracy of the absorption band integral

ratio values. Good agreement (within 15 percent or less) was obtained between experimentally determined mole fractions and the integrated band model for a mixture of two components. For a four-component mixture fair agreement was obtained for the CO and $CO_2$ components (see Table 1), whereas the concentrations determined for $H_2O$ and $N_2$ were not close.

2. The optical constants $n(\nu)$ and $k(\nu)$ of a material can be obtained from reflectance measurements at the interface of a material with vacuum or air. Two types of Kramers-Kronig programs for these calculations were developed.

3. The Kramers-Kronig analysis for finding $k(\nu)$ from $n(\nu)$ values was attempted. Theoretically, this should have been straightforward, but poor results were obtained using the experimental data for $CO_2$.

4. A model was developed and a program written for determining the n's and k's of a thin film on a thick substrate from transmittance measurements. In the past, many film thicknesses were required to achieve these results. This single thickness model gave good results for a CO condensed film except in the region of absorption bands where more work needs to be done.

5. A similar study to the previous one was carried out for determining n's and k's from a single thin film from reflectance measurements. However, the phase angle near infinity $\phi(\infty)$ is not known so this model cannot be used until this value is determined.

6. The problem of finding the optical constants of optical substrate materials at cryogenic temperatures was also investigated briefly. It appears that analysis of the transmittance or reflectance of two substrate thicknesses is the most direct way of determining these properties.

7. The last area investigated was the determination of molecular species concentrations in materials containing more than one infrared-active species from material molar refractivities. The final conclusion of this study was that it appears feasible that an iterative method could be devised such that the molecular concentrations could be obtained for materials containing more than one IR-active specie.

## REFERENCES


1. Querry, M. R., Waring, R. C., Holland, W. E., Earls, L. M., Herrman, M. D., Nijm, W. P., and Hale, G. M. "Optical Constants in the Infrared for $K_2SO_4$, $NH_4H_2PO_4$, and $H_2SO_4$ in Water." *Journal of the Optical Society of America*, Vol. 64, No. 1, January 1974, pp. 39-46.

2. Pimentel, G. C. and McClellan, A. L. *The Hydrogen Bond*. Freeman, San Francisco, California, 1960, Chap. 3, p. 101.

3. Pinkley, L. W., Sethna, P. P., and Williams, D. "Optical Constants of Water in the Infrared: Influence of Temperature." *Journal of the Optical Society of America*, Vol. 67, No. 4, April 1977, pp. 494-499.

4. Arnold, F., Sanderson, R. B., Mantz, A. W., and Thompson, S. B. "Infrared Spectral Reflectance of Plume Species on Cooled Low Scatter Mirrors." AFRPL-TR-73-52 (AD777285), September 1973.

5. Jiang, G. J., Person, W. B., and Brown, K. G. "Absolute Infrared Intensities and Band Shapes in Pure Solid CO and CO in Some Solid Matrices." *Journal of Chemical Physics*, Vol. 62, No. 4, February 1975, pp. 1201-1211.

6. Born, M. and Wolf, E. *Principles of Optics*. Fifth Edition, Pergamon Press, Oxford, 1975.

7. Bowlden, H. J. and Wilmshurst, J. K. "Evaluation of the One-Angle Reflection Technique for the Determination of Optical Constants." *Journal of the Optical Society of America*, Vol. 53, No. 9, September 1963, pp. 1073-1078.

8. Hale, G. M., Querry, M. R., Ruxk, A. N., and Williams, D. "Influence of Temperature on the Spectrum of Water." *Journal of the Optical Society of America*, Vol. 62, September 1972, p. 1103-1108.

9. Ahrenkiel, R. K. "Modified Kramers-Kronig Analysis of Optical Spectra." *Journal of the Optical Society of America*, Vol. 61, No. 12, December 1971, pp. 1651-1655.

10. Schaaf, J. W. "The Infrared Reflectance of Ice I." Ph.D. Thesis, Kansas State University, 1972.

11. Roux, J. A., Wood, B. E., and Smith, A. M. "Infrared Optical Properties of Bipropellant Cryocontaminants." AEDC-TR-79-50, August 1979.

12. Pipes, J. G., Roux, J. A., Smith, A. M., and Scott, H. E. "Transmission of Infrared Materials and Condensed Gases at Cryogenic Temperatures." AEDC-TR-77-71 (AD-A044517), September 1977.

13. Meada, S., Thyagarajan, G., and Schatz, P. N. "Absolute Infrared Intensity Measurements in Thin Films. II. Solids Deposited on Halide Plates." *Journal of Chemical Physics*, Vol. 39, No. 12, December 1963, pp. 3474-3481.

14. Palmer, K. F. and Williams, D. W. "Optical Properties of Water in the Near Infrared." *Journal of the Optical Society of America*, Vol. 64, No. 8, August 1974, pp. 1107-1110; "Optical Constants of Sulfuric Acid; Application to the Clouds of Venus?" *Applied Optics*, Vol. 14, January 1975, pp. 208-219.

## Table 1. Calculated Mole Fractions of Molecular Species in Selected 20 K Cryodeposits

| Mixture (Density ±) | Mol Spec. | Stand. Dens., $\rho_s$, gm/cm$^3$ | Band ID | Band Strength in Mixture: Domain, cm$^{-1}$ | Band Strength in Mixture: $S = \int k d\nu$, cm$^{-1}$ | Band Strength in Mixture: Background, cm$^{-1}$ | Band Strength in Standard: Domain, cm$^{-1}$ | Band Strength in Standard: $S_s = \int k d\nu$, cm$^{-1}$ | Band Strength in Standard: Background, cm$^{-1}$ | $K = S/S_s$ | Mol Mass, M, gm/mole | Calc. Mole Frac. | Chem. Mole Frac. | Newbolt's Mole Fraction |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $N_2/CO_2$ | $CO_2$ | 1.67 | $\nu_3\ ^{13}CO_2$ | 2,270-2,292 | 0.13143 | $-1.0 \times 10^{-7}$ | 2,270-2,292 | 0.46004 | 0.01621 | 0.2857 | 44.01 | 0.296 | 0.253 | 0.394 |
| (1.20 gm/cm$^3$) | $N_2$ | 0.99 | --- | --- | --- | --- | -- | --- | | --- | 28.0134 | 0.704 | 0.747 | 0.606 |
| $N_2/CO$ | CO | 0.95 | $1\leftarrow 0\ ^{13}CO$ | 2,132-2,150 | 0.32869 | $2.0 \times 10^{-5}$ | 2,130-2,156 | 1.73048 | $1.0 \times 10^{-6}$ | 0.1899 | 28.01 | 0.182 | 0.203 | 0.181 |
| (0.99 gm/cm$^3$) | $N_2$ | 0.99 | --- | --- | --- | --- | --- | --- | - | --- | 28.0134 | 0.818 | 0.797 | 0.819 |
| $N_2/H_2O$ | $H_2O$ | 0.931 | $\nu_1,\nu_3,2\nu_2,H_2O$ | 2,910-3,730 | 9.9027 | 0.2460 | 2,900-3,690 | 148.127 | 5.175 | 0.06685 | 18.01534 | 0.111 | 0.123 | 0.0987 |
| (0.84 gm/cm$^3$) | $N_2$ | 0.99 | --- | --- | --- | --- | --- | --- | --- | --- | 28.0134 | 0.889 | 0.877 | 0.9013 |
| $CO_2/CO$ | $CO_2$ | 1.67 | $\nu_3\ ^{13}CO_2$, | 2,270-2,290 | 0.20044 | 0.01973 | 2,2770-2,292 | 0.46004 | 0.01621 | 0.4357 | 44.01 | 0.425 | 0.498 | 0.265 |
| (1.33 gm/cm$^3$) | CO | 0.95 | $1\leftarrow 0\ ^{13}CO$ | 2,078-2,106 | 0.040862 | 0.013669 | 2,084-2,098 | 0.062038 | $7.7 \times 10^{-6}$ | 0.6587 | 28.01 | 0.575 | 0.495 | 0.735 |
| Plume 1 | $CO_2$ | 1.67 | $\nu_3\ ^{12}CO_2$ | 2,320-2,374 | 10.966 | 0.0205 | 2,296-2,396 | 41.2950* | 0 | 0.2656 | 44.01 | 0.1777 | 0.172 | 0.0723 |
| (0.77 gm/cm$^3$) | CO | 0.95 | $1\leftarrow 0\ ^{12}CO$ | 2,132-2,160 | 0.57024* | 0 | 2,130-2,156 | 1.94268* | 0 | 0.2935 | 28.01 | 0.1256 | 0.10 | 0.1862 |
| | $H_2O$ | 0.931 | $\nu_2 H_2O$ | 1,594-1,662 | 0.50419* | 0 | 1,200-2,700 | 20.1201 | 0.0023 | 0.02506 | 18.01534 | 0.0163 | 0.225 | 0.0157 |
| | $N_2$ | 0.99 | | --- | --- | --- | - | --- | -- | --- | 28.0134 | 0.7809 | 0.503 | 0.7258 |

*Band strengths are computed from the Lorentzian decomposition of the data.

# APPENDIX
# PROPAGATION OF ERRORS IN MOLE FRACTION DETERMINATIONS

In the following discussion, the only errors are assumed to be in the ratios of band strengths, R, and in the densities, $\varrho$, of the materials.

*Case 1.* If there are no IR-inactive molecular species in the material and Eq. (10),

$$f_i = \frac{\rho_{si} R_i}{M_i} \Big/ \sum_{\ell=1}^{N} \frac{\rho_{s\ell} R_\ell}{M_\ell}$$

is used, then

$$df_i = \sum_{\ell=1}^{N} \left( \frac{\partial f_i}{\partial R_\ell} dR_\ell + \frac{\partial f_i}{\partial \rho_{s\ell}} d\rho_{s\ell} \right)$$

Now, if $\ell \neq i$,

$$\frac{\partial f_i}{\partial R_\ell} = - \frac{\left(\frac{\rho_{si} R_i}{M_i}\right)\left(\frac{\rho_{s\ell}}{M_\ell}\right)}{\left(\sum_{k=1}^{N} \frac{\rho_{sk} R_k}{M_k}\right)^2} = - \frac{f_i f_\ell}{R_\ell}$$

Also,

$$\frac{\partial f_i}{\partial \rho_{s\ell}} = - \frac{f_i f_\ell}{\rho_{s\ell}}$$

because of the symmetry of the roles of $\varrho_{s\ell}$ and $R_\ell$ in Eq. (10).

If $\ell \neq i$,

$$\frac{\partial f_i}{\partial R_i} = \frac{\frac{\rho_{si}}{M_i}}{\sum_{\ell=1}^{N} \frac{\rho_{s\ell} R_\ell}{M_\ell}} - \frac{\left(\frac{\rho_{si} R_i}{M_i}\right)\left(\frac{\rho_{si}}{M_i}\right)}{\left(\sum_{\ell=1}^{N} \frac{\rho_{s\ell} R_\ell}{M_\ell}\right)^2} = \frac{f_i}{R_i} (1 - f_i)$$

Also

$$\frac{\partial f_i}{\partial \rho_{si}} = \frac{f_i}{\rho_{si}} (1 - f_i)$$

by symmetry. Upon substitution of these partial derivatives into the expression for $df_i$ one obtains, after some algebraic manipulation,

$$\frac{df_1}{f_1} = \frac{dR_1}{R_1} + \frac{d\rho_{s1}}{\rho_{s1}} - \sum_{\ell=1}^{N} f_\ell \left( \frac{dR_\ell}{R_\ell} + \frac{d\rho_{s\ell}}{\rho_{s\ell}} \right)$$

For small errors in $R_\ell$ and $\varrho_{s\ell}$, Eq. (11) follows.

*Case 2.* If only one IR-inactive molecular species (labeled N) is in the material and Eq. (13),

$$f_i = \frac{\rho_{si} R_i}{M_i} \Bigg/ \left( \sum_{\ell=1}^{N-1} \rho_{s\ell} R_\ell \left( \frac{1}{M_\ell} - \frac{1}{M_N} \right) + \frac{\rho}{M_N} \right)$$

is used, then

$$df_1 = \sum_{\ell=1}^{N-1} \left( \frac{\partial f_i}{\partial R_\ell} dR_\ell + \frac{\partial f_i}{\partial \rho_{s\ell}} d\rho_{s\ell} \right) - \frac{\partial f_i}{\partial \rho} d\rho$$

Now, if $\ell \neq i$,

$$\frac{\partial f_i}{\partial R_\ell} = \frac{-\left( \frac{\rho_{si} R_i}{M_i} \right) \rho_{s\ell} \left( \frac{1}{M_\ell} - \frac{1}{M_N} \right)}{\left[ \sum_{\ell=1}^{N-1} \rho_{s\ell} R_\ell \left( \frac{1}{M_\ell} - \frac{1}{M_N} \right) + \frac{\rho}{M_N} \right]^2} = \frac{f_i f_\ell}{R_\ell} \left( \frac{M_\ell}{M_N} - 1 \right)$$

Also,

$$\frac{\partial f_i}{\partial \rho_{s\ell}} = \frac{f_i f_\ell}{\rho_{s\ell}} \left( \frac{M_\ell}{M_N} - 1 \right)$$

by symmetry. If $\ell = i$,

$$\frac{\partial f_i}{\partial R_i} = \frac{\frac{\rho_{si}}{M_i^2} - \left( \frac{\rho_{si}^2 R_i}{M_i} \right) \left( \frac{1}{M_i} - \frac{1}{M_N} \right)}{\left[ \sum_{\ell=1}^{N-1} \rho_{s\ell} R_\ell \left( \frac{1}{M_\ell} - \frac{1}{M_N} \right) - \frac{\rho}{M_N^2} \right]^2} = \frac{f_i}{R_i} \left[ 1 + f_i \left( \frac{M_i}{M_N} - 1 \right) \right]$$

and

$$\frac{\partial f_i}{\partial \rho_{si}} = \frac{f_i}{\rho_{si}} \left[ 1 - f_i \left( \frac{M_i}{M_N} - 1 \right) \right]$$

by symmetry. Also,

$$\frac{\partial f_i}{\partial \rho} = \frac{-\left(\frac{\rho_{si} R_i}{M_i M_N}\right)}{\left[\sum_{\ell=1}^{N-1} \rho_{s\ell} R_\ell \left(\frac{1}{M_\ell} - \frac{1}{M_N}\right) + \frac{\rho}{M_N}\right]^2} = \frac{-f_i}{M_N D} = \frac{-f_i}{\rho} \frac{\rho}{M_N D}$$

where

$$D \equiv \sum_{\ell=1}^{N-1} \rho_{s\ell} R_\ell \left(\frac{1}{M_\ell} - \frac{1}{M_N}\right) + \frac{\rho}{M_N}$$

Now,

$$M_N D = \sum_{\ell=1}^{N-1} \rho_{s\ell} \left(\frac{M_N}{M_\ell} - 1\right) + \rho$$

so

$$\frac{-\rho}{M_N D} = -1 + \sum_{\ell=1}^{N-1} f_\ell \left(1 - \frac{M_\ell}{M_N}\right)$$

and

$$\frac{\partial f_i}{\partial \rho} = \frac{f_i}{\rho} \left[-1 - \sum_{\ell=1}^{N-1} f_\ell \left(1 - \frac{M_\ell}{M_N}\right)\right]$$

After substituting these partial derivatives into the expression for $df_i$ and doing some algebraic manipulation, one finds

$$\frac{df_i}{f_i} = \left[\frac{dR_i}{R_i} + \frac{d\rho_{si}}{\rho_{si}} - \frac{d\rho}{\rho}\right] - \sum_{\ell=1}^{N-1} f_\ell \left(\frac{M_\ell}{M_N} - 1\right) \left[\frac{dR_\ell}{R_\ell} + \frac{d\rho_{s\ell}}{\rho_{s\ell}} - \frac{d\rho}{\rho}\right]$$

For small errors in $R_\ell$, $\varrho_{s\ell}$, and $\varrho$, Eq. (14) follows.

## NOMENCLATURE

| | |
|---|---|
| A | Molar refractivity |
| c | Molar concentration of $i^{th}$ molecular specie |
| f | Mole fraction |
| k | Absorption index |
| M | Molecular mass |
| N | Number density |
| $N_A$ | Avrogadro's number |
| n | Index of refraction |
| P | Cauchy Principle value |
| R | Measured reflectance |
| $\hat{r}$ | Complex reflectivity |
| S | Molecular band strength |
| T | Complex transmission coefficient |
| $\hat{t}$ | Measured transmittance |
| $\alpha$ | Molecular polarizability |
| $\theta$ | Incidence angle |
| $\varrho$ | Density, $gm/m^3$ |
| $\phi$ | Phase shift |

**SUBSCRIPTS**

| | |
|---|---|
| H | High |
| i | Species |
| L | low |
| lib | Librational |

| | |
|---|---|
| $\ell$ | Material |
| N | Species N |
| s | Standard |