

OPTICAL CONSTANTS OF THE MIXTURE OF ICES

T. MUKAI* and W. KRÄTSCHMER

Max-Planck-Institut für Kernphysik, Heidelberg, F.R.G.

(Received 12 November, 1985)

Abstract. The Maxwell–Garnett mixing rule (MG) was applied to estimate the optical constant m^* of the mixture of ices. A fairly good agreement between the resulting values of m^* and those of our laboratory measurements suggests that the MG rule becomes a powerful tool to derive the unknown optical constants of natural dirty-ice, when there are no chemical bonds between the guest and host materials. Our results would provide the knowledge of the optical constants of dirty-ice for studies of icy substances on the surface of satellites, cometary nucleus and interplanetary dust grains based on their reflectance spectra.

1. Introduction

To examine the physical properties of materials for the surfaces of solar system objects covered with icy components based on their reflectance spectra, we need the knowledge of the optical constants of such mixtures of ices in a wide range of wavelengths from UV to far infrared.

There have been several reports concerning the optical constants based on the laboratory measurements for absorbing material, silicate, water-ice and other ices. It is most likely that in nature these components exist as mixtures of several kinds of components. Especially for icy substances, it is widely accepted that the ice (e.g. mainly water-ice because of its higher abundance and higher temperature of condensation) is contaminated by refractory and/or dielectric materials as well as by other icy components, such as NH_3 and CH_4 . Such an inhomogeneous icy material is usually called ‘dirty-ice’ in space.

It is strongly needed to get the optical constants of the dirty-ice in the laboratory measurements for studies of icy substances on the surface of the satellites of the outer planets, the cometary nucleus and also the interplanetary dust grains. However, only a few results have been published up to now (e.g. Fink and Sill (1982), Greenberg *et al.* (1983), and Kitta and Krätschmer (1983)).

An easily understood, there are uncountable combinations of the mixtures of ices, for example, the water-ice with a different degree of dirtiness consisting of different kind of inclusions. Since it seems to be impossible to prepare the complete sets of the optical constants of the mixtures of ices by the laboratory measurements, a theoretical treatment to estimate their optical constants becomes important.

Recently, Mukai and Mukai (1984) have applied the Maxwell–Garnett mixing rule (MG rule) to estimate the values of the complex refractive index m^* for the dirty-ice.

* Permanent address: Kanazawa Institute of Technology, Nonoichi, Ishikawa 921, Japan.

They treated the dirty-ice consisting of water-ice matrix with small size of inclusions of absorbing and silicate grains, which radii should be smaller than the wavelength of interest. Referring to the resulting optical constants of the dirty-ice, the unexpected higher production rate of OH molecules observed in the Comet Bowell (1980b) has been explained by the higher temperature of the dirty-ice grain.

Furthermore, based on the MG rule, Chýlek *et al.* (1983) have shown that the computed spectral albedos of snow on the earth containing carbons as impurities agree well with the field measurements.

In this note, we would like to examine whether an application of the MG rule to the mixture of ices is reasonable or not, based on a comparison between the computed values of m^* and those of our laboratory measurements. Limitations of this making rule will be also mentioned.

2. Effective Optical Constants of the Mixture of Ices

2.1. MAXWELL–GARNETT MIXING RULE

As clarified by Chýlek and Srivastava (1983), the dielectric constant of a composite medium can be deduced based on the MG rule when the matrix material includes the host substance in form of uniformly distributed small impurities. The size of the inclusions should be smaller than or nearly equal to the wavelength λ of interest. Chýlek and Srivastava (1983) have found that the size distribution of inclusions plays an important role in a determination of the effective dielectric constant ϵ_{av} . We will assume, however, that the size of inclusions is very small compared with λ (where λ takes a value from 2.5 μm to 16 μm , and the NH_3 -ice inclusions concerned later are less than 0.1 μm). Therefore, the size distribution of the inclusions can be neglected.

Under the above limitations, the MG rule is expressed for the case of a two-component medium as (e.g. Chýlek and Srivastava, 1983)

$$\epsilon_{av} = \epsilon_m \{ (2\epsilon_m + \epsilon_i - 2f(\epsilon_m - \epsilon_i)) / (2\epsilon_m + \epsilon_i + f(\epsilon_m - \epsilon_i)) \}, \quad (1)$$

where ϵ_m and ϵ_i , respectively, denote the dielectric constants of matrix and inclusion materials, and f means a volume fraction of inclusions to the whole volume of interest. As well known, the dielectric constant in Equation (1) is a complex number and is related to the complex optical constant $m^* = n - i \cdot k$ by $\epsilon = (n^2 - k^2) - i(2nk)$.

2.2. EXPERIMENTAL DATA

The optical constants of the mixtures of ices have been measured by the same procedures as described in Kitta and Krätschmer (1983). Films of binary mixtures of H_2O and NH_3 were condensed from the gas phase onto cold KBr windows (attainable temperature 23–24 K). Using the double beam infrared spectrometer, the reflectivity and transmissivity of films were measured, and subsequently the Kramers–Kronig iteration led the optical constants. Other details of experimental procedures would be referred to Kitta and Krätschmer (1983).

TABLE I

The complex refractive index $m^* = n - i \cdot k$ as a function of wavenumber w for amorphous H₂O ice and NH₃ ice measured at 23 K

w (cm ⁻¹)	H ₂ O ice		NH ₃ ice		w (cm ⁻¹)	H ₂ O ice		NH ₃ ice	
	n	k	n	k		n	k	n	k
4000	1.245	4×10^{-6}	1.400	2×10^{-3}	2500		0.008	1.410	6×10^{-4}
3900	1.241	1×10^{-4}	1.399	4×10^{-6}	2400	1.356		1.408	4×10^{-6}
3800	1.221	4×10^{-4}	1.397	4×10^{-6}	2300	1.348	0.017	1.406	0.001
3700	1.188	0.004	1.394	2×10^{-4}	2200	1.352	0.023	1.404	0.001
3600	1.126	0.023	1.388	0.001	2100	1.349	0.014	1.402	0.002
3550	1.082	0.056	1.382	0.002	2000	1.340	0.010	1.400	0.003
3500	1.034	0.123	1.377	0.004	1900	1.326	0.009	1.398	0.006
3450	1.024	0.236	1.350	0.005	1800	1.303	0.016	1.395	0.003
3400	1.082	0.344	1.283	0.040	1700	1.290	0.068	1.362	0.002
3360	1.157	0.405	1.439	0.136	1675	1.308	0.079	1.355	0.023
3340	1.197	0.428	1.454	0.063	1650	1.326	0.077	1.364	0.051
3320	1.241	0.447	1.432	0.047	1600	1.337	0.060	1.413	0.032
3300	1.290	0.461	1.424	0.049	1500	1.335	0.048	1.400	0.019
3250	1.429	0.454	1.428	0.046	1400	1.331	0.043	1.393	0.014
3200	1.557	0.380	1.453	0.049	1300	1.321	0.036	1.374	0.007
3180	1.595	0.340	1.459	0.029	1200	1.303	0.032	1.311	0.008
3140	1.636	0.236	1.445	0.009	1150	1.289	0.032	1.213	0.071
3100	1.630	0.138	1.436	0.006	1100	1.272	0.033	1.224	0.362
3075	1.606	0.077	1.434	0.005	1050	1.245	0.035	1.703	0.303
3050	1.570	0.045	1.431	0.004	1000	1.201	0.041	1.599	0.010
3000	1.510	0.016	1.426	0.002	950	1.128	0.097	1.512	0.003
2950	1.473	0.007	1.423	0.001	900	1.114	0.218	1.481	0.004
2900	1.447	0.004	1.420	2×10^{-4}	850	1.172	0.322	1.465	0.011
2850	1.430	0.003	1.418	3×10^{-4}	800	1.274	0.395	1.459	0.017
2800	1.414	0.002	1.417	4×10^{-4}	750	1.393	0.404	1.458	0.017
2750	1.403	0.003	1.415	2×10^{-4}	700	1.487	0.362	1.455	0.015
2700	1.392	0.003	1.414	4×10^{-6}	650	1.517	0.279	1.454	0.019
2600	1.376	0.005	1.412	4×10^{-6}					

Optical constant data of pure amorphous H₂O ice, NH₃ ice and the ice of binary mixtures of H₂O with NH₃ in various proportions are listed in Tables I and II. A comparison of these data to other published results is done in Kitta and Krätschmer (1983) for pure H₂O ice. There are no available data at 23–24 K for NH₃ ice and the mixtures of H₂O–NH₃ ice for comparison.

3. Results and Discussion

According to the data of the complex refractive index m^* for pure H₂O ice and NH₃ ice listed in Table I, Equation (1) leads the values of m^* for the mixture of H₂O–NH₃ ice as a function of a volume fraction f of inclusions (NH₃ ice). The H₂O/NH₃ ratios of Table II are referred to the gas-mixture of which the ice was obtained. Due to

TABLE II

The complex refractive index $m^* = n - i \cdot k$ as a function of wavenumber w for the mixture of $\text{H}_2\text{O}-\text{NH}_3$ ices measured at 23 or 24 K. A ratio of H_2O to NH_3 is referred to the volume ratio of gas-mixture of which the ice was obtained

w (cm^{-1})	$\text{H}_2\text{O}:\text{NH}_3 = 2:1$ (24 K)		3:1 (23 K)		4:1 (24 K)	
	n	k	n	k	n	k
4000	1.290	0.002	1.275	0.003	1.270	4×10^{-6}
3900	1.280	0.002	1.264	0.002	1.259	9×10^{-5}
3800	1.265	0.001	1.248	0.003	1.244	4×10^{-4}
3700	1.240	0.004	1.222	0.005	1.217	0.002
3600	1.195	0.014	1.175	0.017	1.167	0.015
3550	1.158	0.035	1.133	0.040	1.131	0.040
3500	1.122	0.089	1.098	0.098	1.094	0.097
3450	1.108	0.166	1.090	0.183	1.087	0.180
3400	1.146	0.289	1.133	0.292	1.128	0.284
3360	1.243	0.299	1.209	0.316	1.202	0.311
3340	1.266	0.297	1.238	0.327	1.231	0.321
3320	1.288	0.304	1.270	0.341	1.261	0.334
3300	1.314	0.311	1.305	0.346	1.296	0.343
3250	1.401	0.305	1.405	0.339	1.395	0.336
3200	1.465	0.250	1.480	0.278	1.477	0.278
3180	1.479	0.221	1.501	0.251	1.495	0.247
3140	1.489	0.170	1.523	0.186	1.517	0.187
3100	1.483	0.129	1.523	0.125	1.519	0.124
3075	1.473	0.106	1.508	0.092	1.505	0.093
3050	1.459	0.092	1.487	0.071	1.486	0.068
3000	1.434	0.087	1.452	0.055	1.448	0.049
2950	1.430	0.090	1.431	0.054	1.425	0.048
2900	1.434	0.087	1.424	0.053	1.416	0.049
2850	1.441	0.078	1.420	0.050	1.412	0.046
2800	1.443	0.062	1.419	0.044	1.409	0.042
2750	1.440	0.046	1.415	0.034	1.406	0.034
2700	1.430	0.036	1.407	0.026	1.400	0.027
2600	1.414	0.021	1.392	0.018	1.386	0.016
2500	1.397	0.016	1.378	0.016	1.371	0.014
2400	1.382	0.019	1.367	0.017	1.360	0.017
2300	1.378	0.027	1.360	0.023	1.355	0.023
2200	1.381	0.027	1.362	0.028	1.357	0.026
2100	1.377	0.017	1.361	0.019	1.355	0.018
2000	1.366	0.015	1.351	0.016	1.346	0.015
1900	1.353	0.015	1.341	0.016	1.335	0.013
1800	1.333	0.022	1.320	0.019	1.313	0.018
1700	1.324	0.057	1.318	0.058	1.307	0.056
1675	1.330	0.067	1.320	0.062	1.315	0.065
1650	1.336	0.077	1.323	0.066	1.323	0.074
1600	1.372	0.065	1.355	0.062	1.355	0.056
1500	1.367	0.051	1.350	0.046	1.342	0.044
1400	1.358	0.035	1.343	0.039	1.336	0.038
1300	1.337	0.031	1.330	0.033	1.323	0.033
1200	1.273	0.035	1.284	0.032	1.285	0.033
1150	1.257	0.106	1.271	0.074	1.273	0.067
1100	1.356	0.142	1.320	0.094	1.313	0.079
1050	1.341	0.045	1.301	0.039	1.289	0.039

Table II (continued)

w (cm ⁻¹)	H ₂ O:NH ₃ = 2:1					
	(24 K)		3:1 (23 K)		4:1 (24 K)	
	n	k	n	k	n	k
1000	1.270	0.070	1.242	0.060	1.239	0.060
950	1.235	0.124	1.204	0.111	1.201	0.104
900	1.232	0.201	1.192	0.188	1.197	0.186
850	1.279	0.281	1.234	0.280	1.218	0.247
800	1.360	0.322	1.314	0.330	1.295	0.334
750	1.456	0.324	1.414	0.344	1.399	0.337
700	1.521	0.266	1.493	0.297	1.477	0.299
650	1.526	0.210	1.507	0.233	1.495	0.235

various fractionation effects of the gas mixture on its way from the storage vessel through pipes and valves into the cryostat, the actual mixing ratio of the condensed ice may deviate from the gas ratio. To check this, we calculated the f -value for the ice mixtures from the MG rule by the following procedure:

$$\Delta n^2 = \sum_{w=w_1}^{w_2} (n_{MG}(w) - n_O(w))^2$$

and

$$\Delta k^2 = \sum_{w=w_1}^{w_2} (k_{MG}(w) - k_O(w))^2$$

are obtained for various values of f by using Equation (1), where the suffixes MG and O denote the results of calculations by the MG rule and of the original measurements of H₂O–NH₃ ice, respectively. The minimum wavenumber $w_1 = 650$ cm⁻¹ and the maximum wavenumber $w_2 = 4000$ cm⁻¹.

Figure 1 shows the results of Δn^2 and Δk^2 for three cases of a mixture of the H₂O–NH₃ ices with various volume fraction of gas-mixtures. The ratio referred to these figures denotes that of gas-mixtures checked in the measurements. Since $f = (\text{a volume of NH}_3 \text{ ice})/(\text{a whole volume of H}_2\text{O–NH}_3 \text{ ice})$, a value of f which gives a minimum value of Δn^2 and/or Δk^2 in Figure 1 seems to correspond to a reasonable ratio expected from the gas-mixtures. For it is likely that the mixture of ices nearly keeps their relative ratio of pure substances in the gas phase. In what follows, we will use a value of f for 0.32 when H₂O:NH₃ = 2:1 in the gas phase, $f = 0.22$ in H₂O:NH₃ : 1 and $f = 0.20$ in H₂O:NH₃ = 4:1.

The resulting values of n and k by the MG rule (filled circles) and those by the measurements (open circles) are illustrated in Figure 2. The computed results based on Equation (1) look like very similar to the measurements, except a slight enhancement of the observed k values in a region of wavenumber $w = 2500 \sim 3000$ cm⁻¹.

As noted by several investigators (see e.g. Fink and Sill, 1982), the gas-mixture of

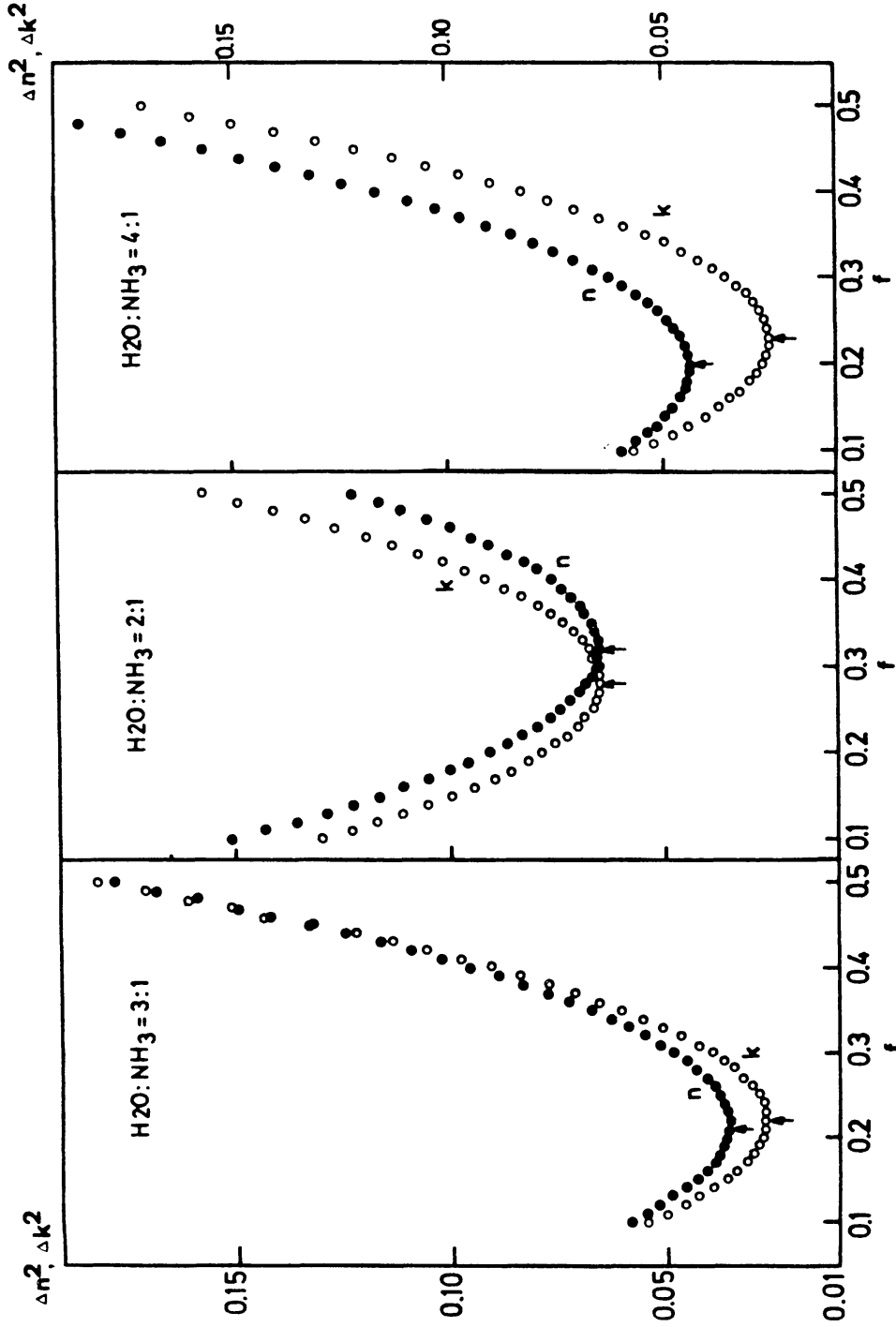


Fig. 1. The symbols of Δn^2 and Δk^2 represent

$$\sum_{w=w_1}^{w_2} (n_{MG}(w) - n_0(w))^2 \quad \text{and} \quad \sum_{w=w_1}^{w_2} (k_{MG}(w) - k_0(w))^2,$$

respectively, where n_{MG} and k_{MG} are the refractive index and absorption coefficient derived by the Maxwell-Garnett mixing rule for the dirty-ice as a function of wavenumber w , and n_0 and k_0 denote those by the laboratory measurements. Here $w_1 = 650 \text{ cm}^{-1}$ and $w_2 = 4000 \text{ cm}^{-1}$. A ratio of H₂O to NH₃ shown in each of figures is referred to the volume of gas-mixture of which the ice was obtained. A value of f means a volume fraction of inclusions, and an arrow indicates a minimum value of Δn^2 or Δk^2 .

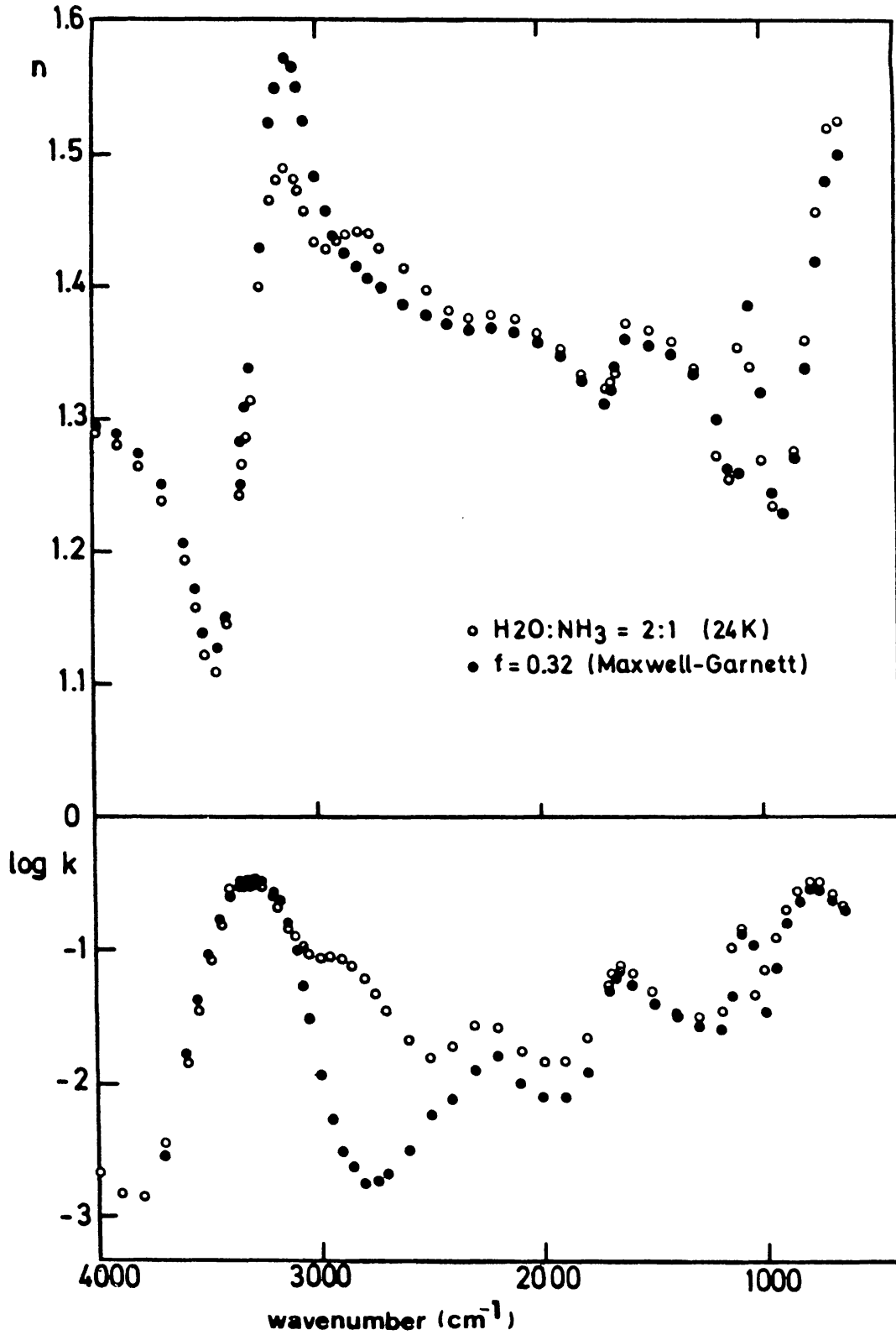


Fig. 2a.

Fig. 2a–c. Refractive index n and absorption coefficient k of the mixture of ices as a function of wavenumber w (cm^{-1}). Open circles show the laboratory measurements at the temperature of 23 or 24 K for a volume ratio of gas-mixture. Filled circles indicate the results computed by the Maxwell–Garnett mixing rule for a volume ratio f of inclusions.

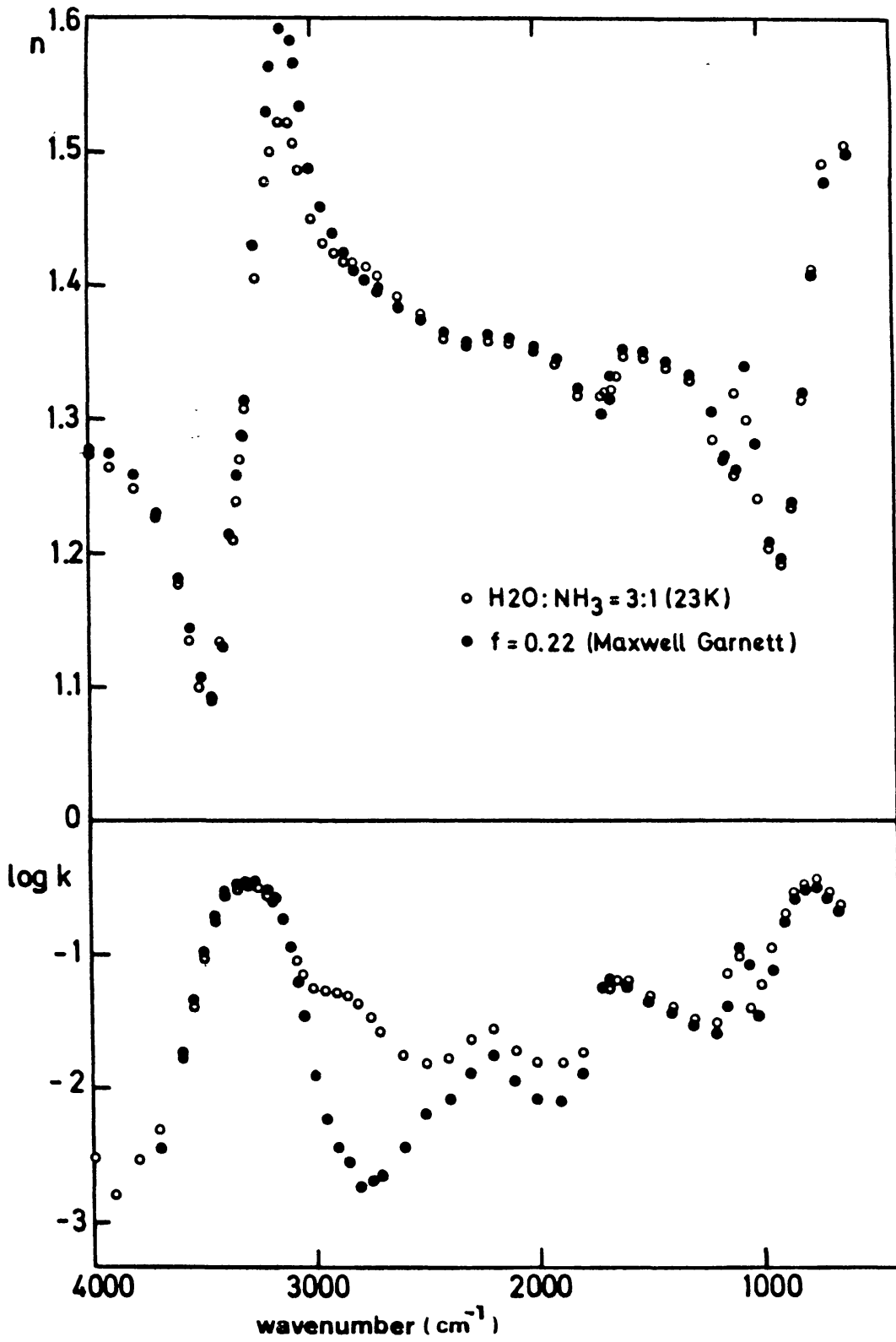


Fig. 2b.

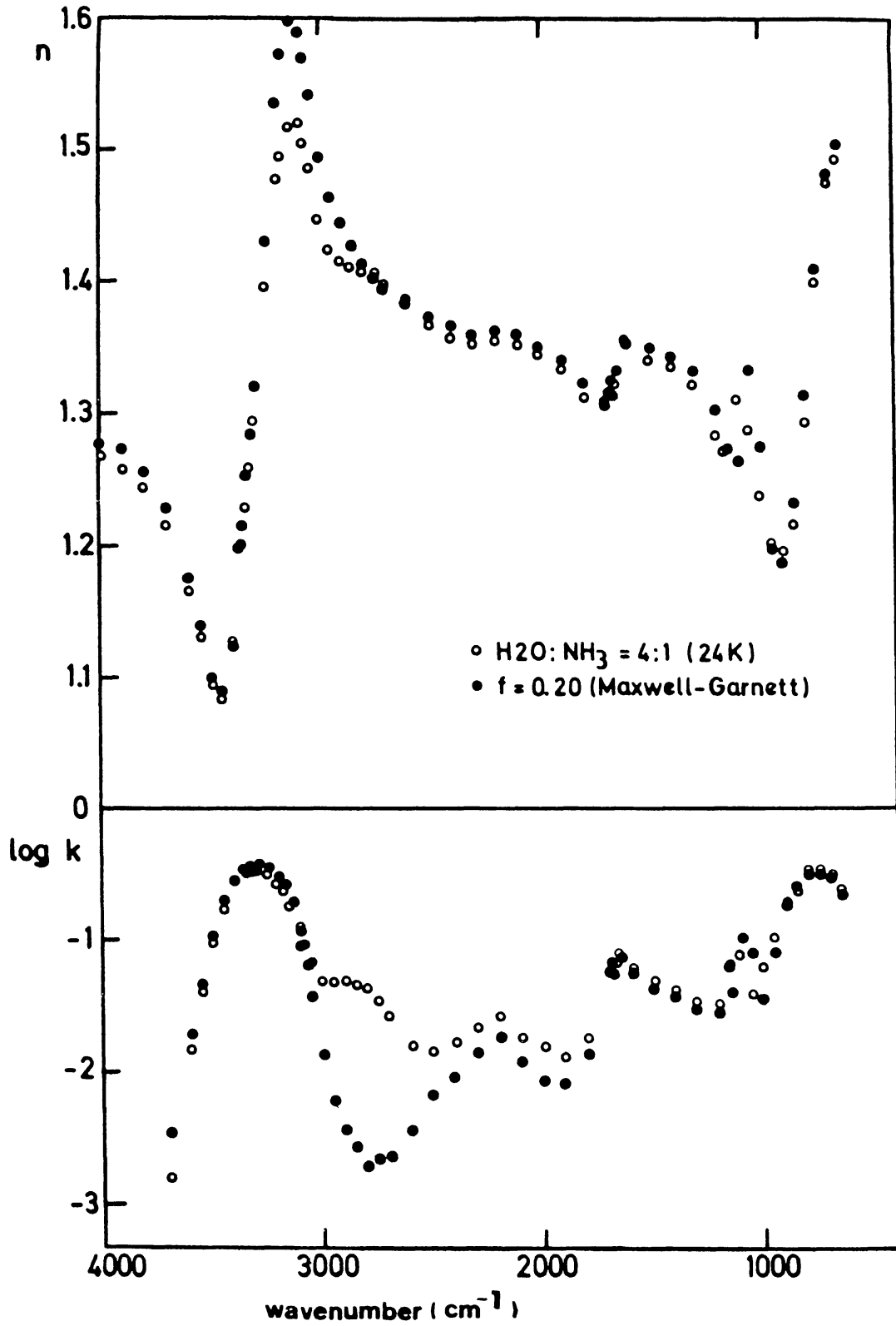


Fig. 2c.

H₂O and NH₃ easily produces ammonia hydrate. Sill *et al.* (1981) have shown that the absorption complex at $\omega \sim 3300 \text{ cm}^{-1}$ detected in a thin film of ammonia hydrate has broken up into three distinct peaks, i.e. (i) NH₃ peak at 3390 cm^{-1} , (ii) water absorption at $\sim 3210 \text{ cm}^{-1}$ and (iii) a new absorption feature at 2915 cm^{-1} . Furthermore, applying X-ray analysis, Bertie and Morrison (1980) have determined the structure of ammonia hydrate and shown that O–H...N bonds absorb between 2910 and 3125 cm^{-1} . Therefore, it is likely that our measured hump of k values in the region of $25000 \sim 3000 \text{ cm}^{-1}$ is caused by the NH₃·H₂O (ammonia monohydrate) produced in the ice sample.

On the other hand, a discrepancy of the n -values at a peak of $\sim 3100 \text{ cm}^{-1}$ in Figure 2 between the estimation by the MG rule and the measurements may come from a different reason. That is, as noted in Bohren and Huffman (1983), Equation (1) might be unfavorable for the mixture of very dissimilar substances. If it would be true, we cannot apply the MG rule to the strong absorption feature of one component in the mixture. A quite well fit of the estimated values of k to the measurements in the same wavenumber region, however, exists as seen in Figure 2. Therefore, we need further comparisons between the measurements of the different kind of ice mixtures and the calculations of the MG rule in the strong absorption peak to derive the conclusions.

In general, the MG rule cannot predict the influence of new chemical products. This implies that when a mixture of several kind of gases produces new chemical compounds, we cannot get a correct optical constant of mixtures of ices. However when the guest material are not chemically bound in the lattice, but only trapped, the MG rule predicts a reasonable optical constant of the mixtures as shown in Figure 2.

In addition, it is known (see Fink and Sill, 1982) that at lower temperatures very little interaction takes place between gases, and then the mixture of ices still keeps the feature of pure substance. Therefore, it might be possible to identify an unknown composition, which is newly produced in the condensation phase of gas-mixture, based on the MG rule.

Acknowledgements

T.M. would like to thank Prof. Fechtig for continuous encouragement, and the Max-Planck-Gesellschaft for financial support during his stay in Heidelberg (F.R.G.). The assistance of Mrs. S. Papp for drawing is kindly acknowledged.

References

- Bertie, J. E. and Morrison, M. M.: 1980, *J. Chem. Phys.* **73**, 4832.
- Bohren, C. F. and Huffman, D. R.: 1983, *Absorption and Scattering of Light by Small Particles*, Wiley, New York.

- Chýlek, P. and Srivastava, V.: 1983, *Phys. Rev.* **B27**, 5098.
- Chýlek, P., Ramaswamy, V., and Srivastava, V.: 1983, *J. Geophys. Res.* **88**, 10837.
- Fink, U. and Sill, G. T.: 1982, in L. L. Wilkening (ed.), *Comets*, Univ. Arizona Press, p. 164.
- Greenberg, J. M., van de Bult, C. E. P. M., and Allamandola, L. J.: 1983, *J. Phys. Chem.* **87**, 4243.
- Kitta, K. and Krätschmer, W.: 1983, *Astron. Astrophys.* **122**, 105.
- Mukai, T. and Mukai, S.: 1984, *Adv. Space Res.* **4**, 207.
- Sill, G., Fink, U., and Ferraro, J. R.: 1981, *J. Chem. Phys.* **74**, 997.