



Universiteit
Leiden
The Netherlands

The temperature dependence of the CO infrared band strength in CO:H₂O ices

Schmitt, B.; Greenberg, J.M.; Grim, R.J.A.

Citation

Schmitt, B., Greenberg, J. M., & Grim, R. J. A. (1989). The temperature dependence of the CO infrared band strength in CO:H₂O ices. *Astrophysical Journal*, 340, L33-L36. Retrieved from <https://hdl.handle.net/1887/6560>

Version: Not Applicable (or Unknown)

License: [Leiden University Non-exclusive license](#)

Downloaded from: <https://hdl.handle.net/1887/6560>

Note: To cite this publication please use the final published version (if applicable).

THE TEMPERATURE DEPENDENCE OF THE CO INFRARED BAND STRENGTH IN CO:H₂O ICES

B. SCHMITT, J. MAYO GREENBERG, AND R. J. A. GRIM

Laboratory Astrophysics, Huygens Laboratory, Leiden University

Received 1988 July 25; accepted 1989 January 18

ABSTRACT

We show that when CO is trapped in water-rich ice mixtures, the 2137 cm⁻¹ (4.680 μm) and 2152 cm⁻¹ (4.645 μm) absorptions undergo irreversible changes in shape upon warmup. If the mixture is warmed up and annealed at $T \approx 115$ K, subsequent changes in strength of the 2134.5 cm⁻¹ (4.685 μm) CO band are reversible with temperature, between 10 and 115 K so that the CO absorption strength is a function of temperature alone and not of history. Both reversible and irreversible effects have important implications in the interpretation of observed absorption bands of solid CO. For annealed interstellar grains, the amount of solid CO embedded in water-rich ice mantles may be underestimated by as much as 40%.

Subject headings: infrared: spectra — interstellar: abundances — interstellar: grains — interstellar: molecules — laboratory spectra — line profiles

I. CO IN INTERSTELLAR ICE MANTLES

Within molecular clouds, the formation of icy mantles on interstellar grains is thought to be the result of various growth processes such as atom surface reactions and molecule condensation. The ice mantles are subjected to such energetic processing as irradiation by UV photons and cosmic rays. The mantles evolve thermally by impulsive heating triggered by grain-grain collisions (Greenberg 1979; d'Hendecourt *et al.* 1982; Schutte 1988) or energetic particles (Léger, Jura, and Omont 1985) as well as by local heating as in accretion disks (Cohen 1983; van de Bult, Greenberg, and Whittet 1985) or in protostellar objects (Lacy *et al.* 1984).

In the interstellar medium CO is the most abundant molecule after H₂. Theoretical calculations using the vapor pressure of pure CO suggested a depletion of gas phase CO molecules by condensation onto cold grains below 17 K in molecular clouds (Duley 1974; Léger 1983; Léger, Jura, and Omont 1985). Furthermore, laboratory experiments have shown (1) the ability to condense a significant fraction of CO molecules mixed with H₂O up to 50 K and (2) that a fraction of CO molecules remains trapped in water ice up to crystallization temperatures (Bar-Nun, Herman, and Laufer 1985; Bar-Nun *et al.* 1987; Schmitt, Grim, and Greenberg 1988a; Sandford *et al.* 1988). To date, solid state CO has indeed been observed in at least 17 objects showing amorphous H₂O absorption (Lacy *et al.* 1984; Whittet, Longmore, and McFadzean 1985; Geballe 1986; Eiroa and Hodapp 1988).

The calculation of column densities of solid state molecules from infrared absorption bands requires the knowledge of the absolute infrared band strengths. The values are often assumed to be independent of the composition, structure, temperature, and history of the ices. A well-known exception to this is solid H₂O where, as a result of hydrogen bond formation, dramatic changes in infrared band shape and strength are observed when compared with the gas phase or matrix isolated H₂O (Hagen, Tielens, and Greenberg 1981, 1983a). This, in fact, allows us to regard the H₂O band as an indicator of the composition and thermal history of interstellar ices (Hagen, Tielens, and Greenberg 1983b). The use of CO as a probe of the temperature and evolution of the ice mantles has been noted by Grim and Greenberg (1987), while Sandford *et al.* (1988)

explicitly demonstrated how the spectral properties of CO may be used as a probe.

For CO an integrated band strength $A_{\text{CO}} = \int \sigma(\nu) d\nu = 1.0 \times 10^{-17}$ cm molecule⁻¹ (σ = cross section), which was measured at 30 K in pure and mixed (argon) matrices (Jiang, Person, and Brown 1975), has generally been used. Sandford *et al.* (1988) showed that the CO band strength is dependent on the matrix in which it is diluted, although such a possibility had also been suggested before (Jiang, Person, and Brown 1975; Person 1981). Sandford *et al.* (1988) measured a value of 1.7×10^{-17} cm molecule⁻¹ for CO in H₂O ice at 10 K, and they used this value or that of pure CO to recalculate the number of solid state CO molecules, N_{CO} , toward 16 sources. We present experimental results on the temperature dependences of the C≡O stretch band of CO in H₂O ices and their possible astrophysical implications.

II. EXPERIMENTAL PROCEDURES

Gas mixtures of CO:H₂O (compositions 1/4 to 1/100) were deposited slowly ($< 5 \mu\text{m hr}^{-1}$) under vacuum (8×10^{-8} mbar) onto a cold (10 K) aluminum block (Hagen, Tielens, and Greenberg 1979). The thicknesses were limited to a maximum of 0.5 μm to avoid scattering. Infrared spectra (4000–400 cm⁻¹) with a resolution of 4 cm⁻¹ (or sometimes 2 cm⁻¹) were recorded in reflection at all temperatures. By assuming symmetric band profiles and measuring the center of the absorption band at one-half and three-quarters of the maximum band depth, the band position could be defined within 0.25 cm⁻¹. We followed the shape and relative intensity evolution of the infrared bands during slow (< 2 K min⁻¹) stepwise warmup from 10 to 110 K (§ III). Following this, the ice mixture was maintained at 115 K for about 1 hr for stabilization, allowing all the CO molecules which were not firmly trapped in the H₂O ice matrix to evaporate. After recooling to 10 K we are able to use the known values of A_{CO} and $A_{\text{H}_2\text{O}}$ at this temperature to calculate the remaining CO fraction. After stabilization the sample evolved very slowly with a CO loss rate at 100 K of at most 0.02% per hour relative to H₂O (Schmitt, Grim, and Greenberg 1988a, b). We are thus able to measure the evolution of the CO infrared band intensity as a function of temperature at constant ice composition during recooling and

subsequent warmup, each in steps of 5 K (§ IV). In one experiment *three complete cycles* confirmed the reversibility found in the first one. The possibility of CO recondensation on the sample during recooling has been eliminated by using different heating procedures and by noting that only a very small recondensation occurs with pure CO samples.

The CO integrated band areas under a straight baseline, $I_{\text{CO}}(T)$, were calculated over a defined frequency range. By varying the frequency range the accuracy in $I_{\text{CO}}(T)$ was estimated to be better than 0.005 cm^{-1} ($< 5\%$ of the band area). For the error bars shown in Figure 2 we have used the statistical error after averaging seven CO:H₂O experiments. After each 5 K step in the cooling/heating cycle the integrated CO band intensity $I_{\text{CO}}(T)$ at temperature T was measured and normalized to the integrated intensity at 10 K using the ratio $I_{\text{CO}}(T)/I_{\text{CO}}(10 \text{ K})$.

III. EVOLUTION OF THE CO BAND SHAPE

Where comparable, our experimental results on the spectral properties of CO in H₂O ices are generally in good agreement with those published by Sandford *et al.* (1988). We cover, however, a wider range of compositions. The infrared C≡O stretching region of the sample consists of two overlapping absorption bands peaking at about 2137 and 2152 cm^{-1} . The position and the full width at half-maximum (FWHM) of the peak around 2137 cm^{-1} vary with composition (Table 1). For all CO/H₂O ratios studied, the 2152 cm^{-1} band accounts for 22%–26% of the total integrated intensity of the bands. When the deposition is made at a higher temperature, the $2152/2137 \text{ cm}^{-1}$ band intensity ratio is reduced with respect to the ratio measured at 10 K.

A progressive and *irreversible* decrease of the 2152 cm^{-1}

TABLE 1
PEAK POSITION AND FWHM OF CO
IN WATER ICE AT 10 K

[CO]/[H ₂ O]	ν (cm^{-1})	$\Delta\nu$ (cm^{-1})
∞	2138.50	2.0
25%	2138.25	11.8
20	2137.75	11.2
15	2137.00	10.8
8.5	2136.50	10.5
3.5	2136.25	9.5
1	2135.75	7.5

NOTE.—The frequencies and FWHMs refer to the main CO absorption band. The [CO]/[H₂O] ratios were calculated using $A_{\text{CO}} = 1.7 \times 10^{-17} \text{ cm molecule}^{-1}$ (Sandford *et al.* 1988) and $A_{\text{H}_2\text{O}} = 1.7 \times 10^{-16} \text{ cm molecule}^{-1}$.

band intensity occurs upon the first heating. It has disappeared completely at 115 K (Fig. 1). Due to diffusion and evaporation of CO the main band near 2137 cm^{-1} also decreases, but at a much slower rate and is still present at 120 K (Schmitt, Grim, and Greenberg 1988a, b; Sandford *et al.* 1988). Heating to 100 K *irreversibly* shifts the band position to 2134.5 cm^{-1} and the FWHM is decreased to 7.0 cm^{-1} (Fig. 1). Except for the intensity changes discussed in the next section, recooling at 10 K has minor effects on the FWHM of the CO band ($< 0.5 \text{ cm}^{-1}$).

IV. TEMPERATURE DEPENDENCE OF THE CO BAND STRENGTH

The measurements of the band intensities have only been performed for CO:H₂O ices annealed for a long time at 115 K

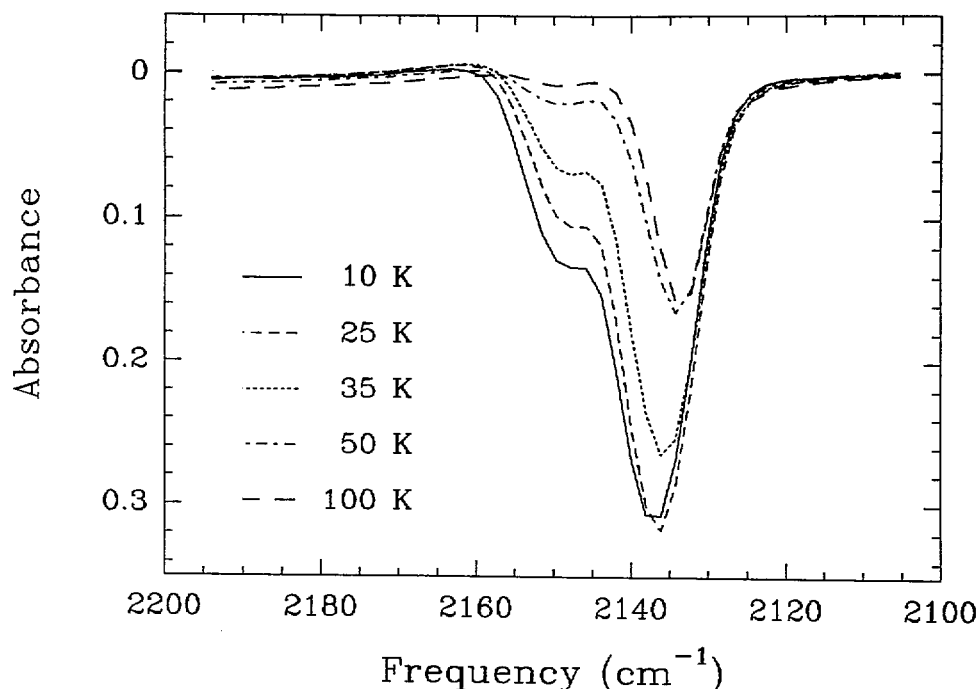


FIG. 1.—Irreversible evolution of the position and shape of the 2137 and 2152 cm^{-1} CO absorption bands in H₂O ice with temperature. All IR spectra were recorded at 10 K with a 4 cm^{-1} resolution. The IR spectra after deposition at 10 K (CO/H₂O = 25%) and after heating to 25 K (23.5%), 35 K (18.5%), 50 K (9.5%), and 100 K (7.5%), respectively, are shown.

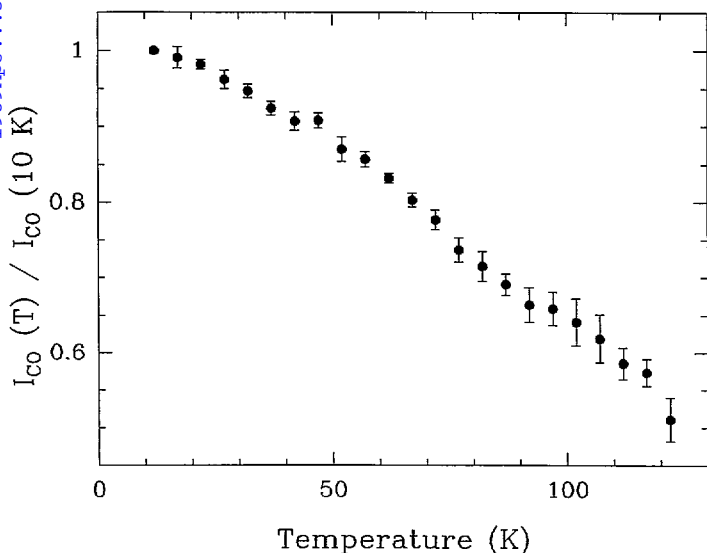


FIG. 2.—The integrated band intensity $I_{\text{CO}}(T)$ of the 2134.5 cm^{-1} CO band, after normalizing to the intensity at 10 K [$I_{\text{CO}}(10 \text{ K})$], vs. temperature. The data were averaged over seven experiments with stabilized CO/H₂O ratios between 1% and 10%. The error bars represent the standard deviations.

(§ II). For these stable annealed mixtures containing less than 10% CO relative to H₂O, the 2152 cm^{-1} CO satellite was not present. Figure 2 shows the *reversible* change of the 2134.5 cm^{-1} CO integrated band intensity (and CO band strength) *without* affecting the band profile. The observed reversibility is independent of the CO concentration, at least for stabilized CO/H₂O ratios lower than 10%. An intensity decrease to 60% of $I_{\text{CO}}(10 \text{ K})$ is observed when the temperature is raised from 10 to 100 K.

The reversible character of band intensities has also been found for CH₄:H₂O and, possibly, CO₂:H₂O ices (Schmitt, Grim, and Greenberg 1988b), but not for CO:NH₃ and CO:CH₃OH ices. For the C=O stretching mode of CO₂ (2340 cm^{-1}) only a small temperature-dependent intensity effect was found [$I_{\text{CO}_2}(100 \text{ K})/I_{\text{CO}_2}(10 \text{ K}) \approx 0.95$], but for the bending mode of CH₄ (1300 cm^{-1}) the temperature effect is as large as for CO. Similarly, for the C—H stretching mode of CH₄ (3010 cm^{-1}) a significant decrease is observed, but the blending with the broad H₂O band makes an accurate measurement difficult.

V. INTERPRETATION

The presence and the evolution of the two CO bands was interpreted by Sandford *et al.* (1988) on the basis of the trapping of CO molecules in two physically different types of sites. In the following we will outline an alternative interpretation of the CO infrared spectral features based on other types of interactions but in a single type of site. A detailed discussion of this model will be published later (see Grim 1988).

Condensation of H₂O-rich mixtures at low temperature produces a *highly disordered amorphous solid* with an *incomplete hydrogen-bonding network* (Ritzhaupt, Smyrl, and Devlin 1976; Gilberg, Hanus, and Foltz 1982). In such a solid, the molecules are frozen in random orientations with a certain statistical fraction of favorably orientated CO forming CO—H₂O complexes. The assignment of the 2152 cm^{-1} satellite to a hydrogen-bonded complex of H₂O and CO is consistent with the increase of the absorption frequency of the CO—H₂O complex in CO:H₂O ices with increasing H₂O concentration

(Hagen and Tielens 1981). The frequency shift to 2152 cm^{-1} of this complex in H₂O ice with respect to 2149 cm^{-1} in argon (Dubost 1976) or 2146.5 cm^{-1} in CO (Hagen and Tielens 1981) is not fully understood, but it is possible that the simultaneous interaction of the water molecule in the CO—H₂O complex with other water molecules causes this shift. The constant 2152/2137 cm^{-1} band intensity ratio (22%–26%) observed at 10 K for the limited range of compositions studied (1% < CO/H₂O < 25%) could be the result of the statistically orientated CO molecules relative to the free, or very weakly bonded, O—H groups in the hydrogen-bonded network. Such groups, as evidenced in our experiments by an absorption band at 3630 cm^{-1} , are the result of nonpolar inclusions (Ritzhaupt, Smyrl, and Devlin 1976). The frequency shift with respect to the positions of such groups in Ar:H₂O matrices, 3650 cm^{-1} for 12% < H₂O/Ar < ∞ (Ritzhaupt, Smyrl, and Devlin 1976) and 3700 cm^{-1} for H₂O/Ar < 3% (van Thiel, Becker, and Pimentel 1957) indicates the weak bonding.

The simultaneous disappearance upon annealing of the 2152 cm^{-1} satellite band and the 3630 cm^{-1} H₂O band are explained by the rearrangement of the CO—H₂O bonds into the more energetically favorable H₂O—H₂O bonds of H₂O ice. The assignment of the 2152 cm^{-1} satellite to a hydrogen-bonded complex of H₂O and CO is supported by the *good correlation* between the irreversible decrease upon warmup of the 2152 cm^{-1} and the weak 3630 cm^{-1} bands. The displacement of a CO molecule from an interstitial site into a substitutional site during annealing, as suggested by Sandford *et al.* (1988), seems rather unlikely since not only is the breaking of hydrogen bonds between water molecules required, but also water molecule displacement. As a matter of fact, annealing of amorphous H₂O ice leads to just the opposite behavior (Ritzhaupt, Smyrl, and Devlin 1976; Hagen, Tielens, and Greenberg 1983b).

A possible explanation for the temperature dependence of the integrated band strength of the 2134.5 cm^{-1} CO band can be the effect of dipolar interactions between CO and H₂O molecules (see Grim 1988), but it is clear that any model involving a hydrogen bond between CO and H₂O cannot be adequate for explaining the temperature changes of the 2134.5 cm^{-1} band.

VI. ASTROPHYSICAL IMPLICATIONS

The implications of the influences of environment and temperature on the CO band positions in interstellar grain mantles have been discussed by Sandford *et al.* (1988). Here we restrict ourselves by noting that the CO absorption consists of two overlapping bands around 2137 cm^{-1} (4.680 μm) and 2152 cm^{-1} (4.645 μm) with spectral properties depending on the temperature, composition and history of the dust (see Table 1 and Fig. 1).

The CO and H₂O ice band shapes show some specific irreversible changes during a first warmup and some reversible effects upon subsequent cooling/heating cycles. Although the H₂O band *strength* is almost unaffected by temperature, the CO band strength shows extensive reversible changes. The combination of the two, CO and H₂O, somewhat independent spectral probes can provide information about the composition and thermal history of the grains. We note particularly that the presence or absence of the 2152 cm^{-1} satellite, or the 3630 cm^{-1} (2.755 μm) O—H band, might reveal the temperature evolution and structure of the grain mantles. So far, the 2152 cm^{-1} band has not been observed, either because this

band is too weak or because its position overlaps with a Pfund- β emission line (Geballe 1986). The 3630 cm^{-1} band is unfortunately obscured by atmospheric H_2O absorption but is a *prime* candidate for ISO.

There are good indications, mainly from the $3.1\text{ }\mu\text{m}$ band shape, that some of the ice mantles observed in space are at, or have been heated to, fairly high temperatures (50–80 K) (Hagen, Tielens, and Greenberg 1983b; van den Bult, Greenberg, and Whittet 1985; Forveille *et al.* 1987). Perhaps, in certain environments such as around protostellar nebulae, hot molecular clouds or circumstellar envelopes, volatile molecules like CO can be trapped in relatively hot H_2O ices (Bar-Nun, Herman, and Laufer 1985; Schmitt, Grim, and Greenberg 1988a). In such cases, the value of the integrated band strength of CO in H_2O ices measured at 10 K is no longer valid and the temperature effect on A_{CO} must be taken into account. The combination of our *relative* strength measurements (Fig. 2) with the *absolute* one, $1.7 \times 10^{-17}\text{ cm molecule}^{-1}$ at 10 K, from Sandford *et al.* (1988) makes it possible to define the CO band strength at each temperature between 10 and 115 K.

Considering icy grain mantles which start with a CO/ H_2O ratio of 20% at 10 K, thermal cycling which consists of heating to 80 K followed by cooling to 10 K decreases the CO fraction to about 8% (Schmitt, Grim, and Greenberg 1988b). The use of the CO band strength measured at 10 K for such processed ice mixtures would give a correct value of the solid CO abundance. Considering the same grains subjected to the same heating *but* without recooling (as generally expected for protostellar nebulae) the use of the CO band strength measured at

10 K would give a value of *only* 5.5% thus underestimating the true CO fraction by 30%.

VII. CONCLUDING REMARKS

When calculating CO column densities toward interstellar IR sources one should take the thermal effects into account, especially if water ice is present. More precisely, the correction for the band strength requires knowledge of the temperature distribution of grains in the line of sight to the object. However, the wide range in the astrophysical solid CO peak positions ($2134\text{--}2141\text{ cm}^{-1}$) and FWHM ($5\text{ to }12\text{ cm}^{-1}$) are far from well understood (see Sandford *et al.* 1988, Table 4). It is now quite clear that simple unprocessed CO: H_2O ices cannot account for this wide range of CO band shapes. On the other hand, the spectroscopic properties described in this *Letter* for CO: H_2O ices are certainly not restricted to CO in this simple ice mixture. They could also be very important for other molecules, radicals, or ions condensed or synthesized in grain mantles. Photoprocessing must play a role.

Therefore, further laboratory experiments are necessary to improve our understanding of the very complex chemical and physical interactions in solid molecular mixtures. Such studies with various astrophysically relevant molecules will be of particular interest for the interpretation of the sensitive and high-resolution spectra from ISO.

The authors thank Dr. M. S. de Groot for many stimulating discussions. B. Schmitt gratefully acknowledges support from the European Space Agency in the form of an E.S.A. fellowship.

REFERENCES

- Bar-Nun, A., Herman, G., and Laufer, D. 1985, *Icarus*, **63**, 317.
 Bar-Nun, A., Dror, J., Kochavi, E., and Laufer, D. 1987, *Phys. Rev. B*, **35**, 2427.
 Cohen, M. 1983, *Ap. J. (Letters)*, **270**, L69.
 d'Hendecourt, L. B., Allamandola, L. J., Bass, F., and Greenberg, J. M. 1982, *Astr. Ap.*, **109**, L12.
 Dubost, H. 1976, *Chem. Phys.*, **12**, 139.
 Duley, W. W. 1974, *Ap. Space Sci.*, **26**, 199.
 Eiroa, C., and Hodapp, K.-W. 1988, *Astr. Ap.*, in press.
 Forveille, T., Morris, M., Omont, A., and Likkell, L. 1987, *Astr. Ap.*, **176**, L13.
 Geballe, T. R. 1986, *Astr. Ap.*, **162**, 248.
 Gilberg, E., Hanus, M. J., and Foltz, B. 1982, *J. Chem. Phys.*, **76**, 5093.
 Greenberg, J. M. 1979, in *Stars and Star Systems*, ed. B. E. Westerlund (Dordrecht: Reidel), p. 173.
 Grim, R. J. A. 1988, Ph.D. thesis, University of Leiden, The Netherlands.
 Grim, R. J. A., and Greenberg, J. M. 1987, *Astr. Ap.*, **181**, 155.
 Hagen, W., and Tielens, A. G. G. M. 1981, *J. Chem. Phys.*, **75**, 4198.
 Hagen, W., Tielens, A. G. G. M., and Greenberg, J. M. 1979, *Ap. Space Sci.*, **65**, 215.
 ———. 1981, *Chem. Phys.*, **56**, 367.
 ———. 1983a, *Astr. Ap. Suppl.*, **51**, 389.
 ———. 1983b, *Astr. Ap.*, **117**, 132.
 Jiang, G. J., Person, W. B., and Brown, K. G. 1975, *J. Chem. Phys.*, **62**, 1201.
 Lacy, J. H., Baas, F., Allamandola, L. J., Persson, S. E., McGregor, P. J., Lonsdale, C. J., Geballe, T. R., and van de Bult, C. E. P. 1984, *Ap. J.*, **276**, 533.
 Léger, A. 1983, *Astr. Ap.*, **123**, 271.
 Léger, A., Jura, M., and Omont, A. 1985, *Astr. Ap.*, **144**, 147.
 Person, W. B. 1981, in *Matrix Isolation Spectroscopy*, ed. A. J. Barnes *et al.* (Dordrecht: Reidel), p. 415.
 Ritzhaupt, G., Smyrl, N., and Devlin, J. P. 1976, *J. Chem. Phys.*, **64**, 435.
 Sandford, S. A., Allamandola, L. J., Tielens, A. G. G. M., and Valero, G. J. 1988, *Ap. J.*, **329**, 498.
 Schmitt, B., Grim, R. J. A., and Greenberg, J. M. 1988a, in *Experiments on Cosmic Dust Analogues*, ed. E. Bussoletti *et al.* (Dordrecht: Kluwer), p. 259.
 ———. 1988b, in *Dust in the Universe*, ed. M. E. Bailey and D. A. Williams (Cambridge: Cambridge University Press), p. 291.
 Schutte, W. A. 1988, Ph.D. thesis, University of Leiden, The Netherlands.
 van de Bult, C. E. P. M., Greenberg, J. M., and Whittet, D. C. B. 1985, *M.N.R.A.S.*, **214**, 289.
 van Thiel, M., Becker, E. D., and Pimentel, G. C. 1957, *J. Chem. Phys.*, **27**, 486.
 Whittet, D. C. B., Longmore, A. J., and McFadzean, A. D. 1985, *M.N.R.A.S.*, **216**, 45P.

J. M. GREENBERG and R. J. A. GRIM: Laboratory Astrophysics, Huygens Laboratory, Leiden University, P.O. Box 9504, 2300 RA Leiden, The Netherlands

B. SCHMITT: Laboratoire de Glaciologie et Géophysique de l'Environnement, 2 rue Molière, B.P. 96, 38402 Saint Martin d'Hères Cedex, France