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LABORATORY EXPERIMENTS ON CARBONACEOUS MATERIAL AS A SOURCE FOR THE RED RECTANGLE VISUAL EMISSIONS

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ABSTRACT

We have subjected mixtures of CO, Ar, N_2, H_2O, and CH_4 with 42% and 8% argon to an electrical discharge, frozen out the reaction products at $T \sim 20$ K, and subsequently warmed the sample to room temperature. This has resulted in a stable residue having broad-band fluorescence. It is suggested that interstellar grains in the Red Rectangle/HD 44179 are coated with a residue of generally similar composition that is responsible for the broad emission feature in the 5400–7500 Å spectral region.

Subject headings: interstellar: grains — interstellar: matter — nebulae: individual (Red Rectangle)

I. INTRODUCTION

The optical spectrum of the Red Rectangle bipolar nebula surrounding HD 44179 exhibits a broad band of emissions upon which are superposed narrower emission features which are of probable molecular origin (Schmidt, Cohen, and Margon 1980; Warren-Smith, Scarratt, and Mardin 1981; Wdowiak 1981). Webster (1979) has suggested that the broad feature is due to Doppler broadening in a manner similar to SS 433; however, VLA observations (Geldzahler and Cohen 1983) cast doubt on that hypothesis. The most probable origin for the broad feature between 5400 Å and 7500 Å is therefore molecular (Schmidt *et al.* 1980; Perkins *et al.* 1981). Greenstein and Oke (1977) in their analysis of the spectrum of the Red Rectangle concluded that an extreme and unusually high red albedo of the grains or else fluorescence is required for the emission band. We report here results of experiments that support the fluorescence mechanism (Donn *et al.* 1984). These initial results are very suggestive in supporting the fluorescence mechanism, although additional work is needed which may provide more definite agreement for, or show serious problems with, the fluorescence hypothesis.

II. EXPERIMENTAL PROCEDURE

A mixture of gas reagents considered to be representative constituents of the more abundant elements in the interstellar medium was prepared in an evacuated 1 liter glass bulb at a total pressure of 400 torr. The constituents of the chosen mixture were CO, CH_4, N_2, H_2O, and Ar. Laboratory simulations of cosmic ices have almost exclusively used molecular mixtures of H, C, N, and O. However, cosmic abudance tables, e.g., Cameron (1982) show a ratio $H/Ar = 2.7 \times 10^5$, which compares well with the molecular ratio of $H_2/CO = 10^6$ in the low-density Ophiuchus cloud (Black and Dalgarno 1977) and 10^4 in dense clouds (Thaddeus 1977; Guelin 1985). Further, Ar and CO have nearly identical volatilities (Honig and Hook 1960; Weast 1983). This indicates that grain mantles would have more or less comparable amounts of Ar and CO. The ratio of argon to total reactive elements may be approximately cosmic for the samples with the lower argon concentration if the total C + O + N abundance is depleted by a factor of 10 through inclusion in grains (Snow 1975). The higher argon concentration will give some indication of the effect of partial matrix isolation during deposition. However, as we examined the residue after warming to room temperature and did not examine the low temperature deposit, the argon was not expected to have much effect. As the fluorescence measurements show, this was, indeed, the case. A nonvolatile residue of a cosmic mixture of gases had properties that could account for the observed visual features of the Red Rectangle. The abundance ratio of elements forming a grain is unknown and cannot be accurately estimated. HD 44179, the exciting star for the Red Rectangle, is embedded in a dense circumstellar cloud which prominently displays emission feature at 3.3–3.4, 6.1, 7.8, 8.6, and 11.2 μm (Merrill 1988; Aitken *et al.* 1979). These bands are now generally attributed to carbonaceous material of some form, although no definite identification has been made. It seems reasonable to adopt a carbon-rich composition for these simulations.

The C:O:N ratio in the experimental mixture is about what is expected for HD 44179. H_2O was introduced as a liquid into the bulb; its partial pressure was determined by the ambient temperature. The other constituents were introduced as gases and the partial pressure measured with a manometer. Two types of starting mixtures were used. The first had a high (42%) concentration of argon, $Ar:CO:N_2:CH_4:H_2O = 170:170:21:18:20$, and the second a low (8%) argon concentration, $Ar:CO:N_2:CH_4:H_2O = 19:170:20:18:20$. The numbers are the partial pressures of the components in torr. At termination, the total pressure was 300 torr. Because the H_2O partial pressure was constant, its relative abundance was correspondingly greater at termination. The gases were passed through a capillary tube into a linear discharge tube attached to the metal vacuum jacket of an Air Products Model 202 closed cycle refrigerator. A high-frequency Tesla coil excited a discharge between one end of the discharge tube and the vacuum jacket at the other end. Products of reactions in the plasma flowed out of the end of the tube, through an aperture in the radiation shield at $T \simeq 50$ K, and condensed upon a sapphire substrate at $T < 20$ K. The temperature was monitored by a silicon diode sensor installed in the base of the substrate holder. Gas flow was adjusted to keep the measured temperature at $T = 15$ K during the discharge.

Initial experiments indicated that if the gas flow were too great then unstable concentrations of radicals would build up. This resulted in exothermic reactions and a thermal runaway, usually within 15 minutes, that caused a large loss of material from the deposit. By careful monitoring of the temperature and control of the gas flow a deposit could be prepared over a period of 4 h. Upon completion of deposition the temperature of the sample was slowly raised in a controlled fashion. At a threshold temperature near 20 K the trapped radicals began to react. This rapidly raised the temperature to ~50 K, causing reactions among all condensed plasma products and the production of light flashes in the film. After the reaction phase of the experiment was completed, the samples were warmed to room temperature overnight in vacuum. A yellow residue could be seen on the side of the sapphire substrate that faced the discharge.

Three samples of residues from high argon concentration mixtures were prepared. Samples A and B were made at Goddard. Sample A was too spotty for a reproducible spectrum to be measured. Sample C was prepared several months later at the University of Alabama, Birmingham (UAB). A low-argon sample (D) was prepared at the same time at UAB. Both samples were sent to Goddard for measurement of their fluorescent quantum efficiency.

An absorption spectrum of the residue between 200 nm and 600 nm was obtained at room temperature using a Cary 14 double beam spectrometer. The spectrum is shown in Figure 1. The absorbance increases with decreasing wavelength for which scattering in the film is probably a major contributor, and a "knee" appears at ~250 nm. The samples were found to be fluorescent, and spectra of the emission were obtained by two methods. (1) The sample was excited with a Xenon light source/monochrometer combination, and the spectrum of the fluorescence was recorded with an optical multichannel analyzer (OMA). (2) The sample was excited with a pulsed N_2 laser at 337 nm, and the spectrum of the fluorescence recorded with a scanning spectrometer. The first technique allowed excitation in bands ~25 nm FWHM (full width at half-maximum), between 300 nm and 475 nm. The excitation component could be subtracted to reveal the fluorescence. The large reduction in scattered light with the highly collimated, small laser beam made it possible to obtain spectra with the sample cooled by

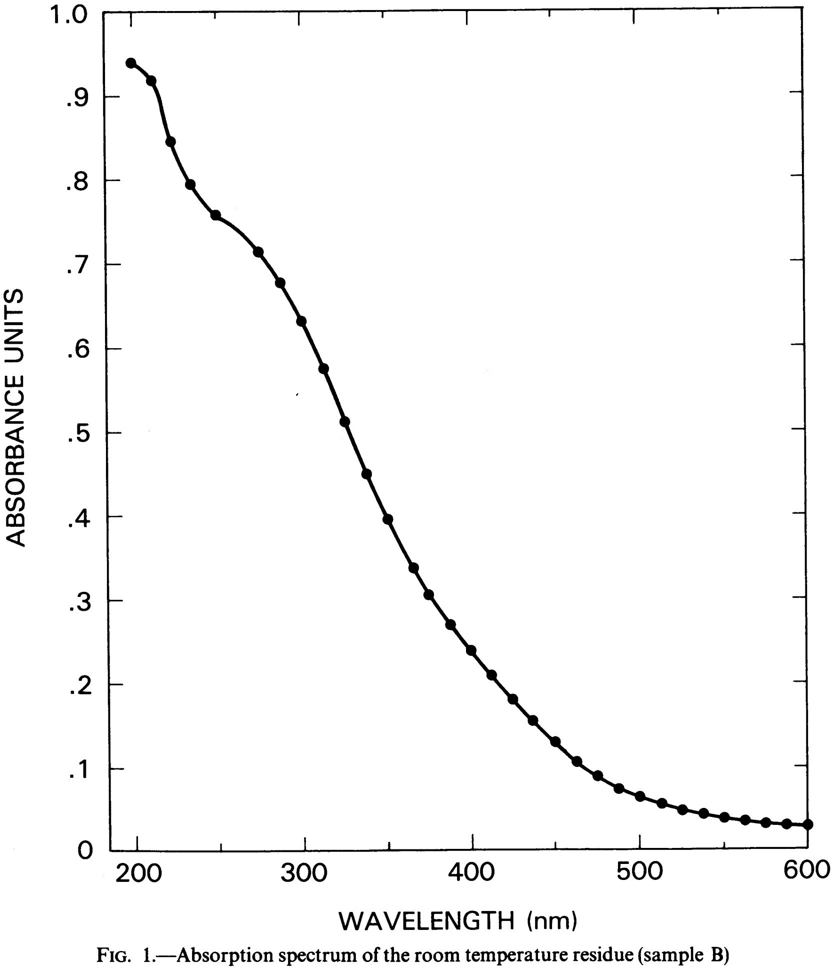

FIG. 1.—Absorption spectrum of the room temperature residue (sample B)

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liquid nitrogen at a nominal temperature of 77 K using 337 nm excitation. The spectra obtained by each technique were corrected for the quantum efficiency of the detectors. The absolute quantum efficiencies of fluorescence for samples C and D were measured using as a standard riboflavin, which has a fluorescence efficiency of 0.25.

III. RESULTS

The fluorescence spectrum of a high argon residue (sample B) excited by the Xenon lamp/monochrometer combination at 300 nm is given in Figure 2. Excitation at $\lambda > 300$ nm shifts the blue cutoff of the fluorescence to longer wavelengths but does not significantly effect the shape of the red cutoff. The fluorescence spectra of the two high-argon samples obtained by laser excitation at 337 nm are presented in Figure 3. All of the spectra in Figures 2 and 3 display fluorescent intensity distributions of ~200 nm FWHM. Laser excited spectra seemed to have less structure than did the Xenon lamp/monochrometer–excited spectra. However, because of the much higher noise level in the lamp-excited spectra, some of the structure seen in Figure 2 may be spurious. The feature at 500 nm seen in Figure 3 is introduced by the spectrometer.

Fluorescence from sample B was centered near 500 nm when excited at 300 nm, at room temperature by the broad-band lamp/monochrometer combination. The peak shifted to 560 nm when excited by the 337 nm laser line at room temperature and moved further to the red; i.e., to 575 nm, when excited by the 337 nm laser line at 77 K. Sample A showed a central peak near 590 nm as well as evidence for a smaller peak centered near 430 nm when excited by the 337 nm laser line at room temperature. A peak at 430 nm also appears in the spectrum of sample B excited by the Xenon lamp/monochrometer source. We also observe smaller peaks near 480 nm, 520 nm, and 570 nm. Only the major peak at 480 nm is definitely real. Cooling to liquid nitrogen temperature increased the fluorescent intensity of sample B by a factor of 2.

The absolute quantum efficiencies for fluorescence for samples C and D are given in Table 1. These results are estimated to have an uncertainty of about 25 percent. The data in Table 1 shows that cooling a residue to liquid nitrogen temperature substantially increases the fluorescence efficiency. For sample C, from a high argon mixture, this is a factor of 2, the same as found in the measurement of the spectra. In the case of sample D from the low argon mixture, the room temperature

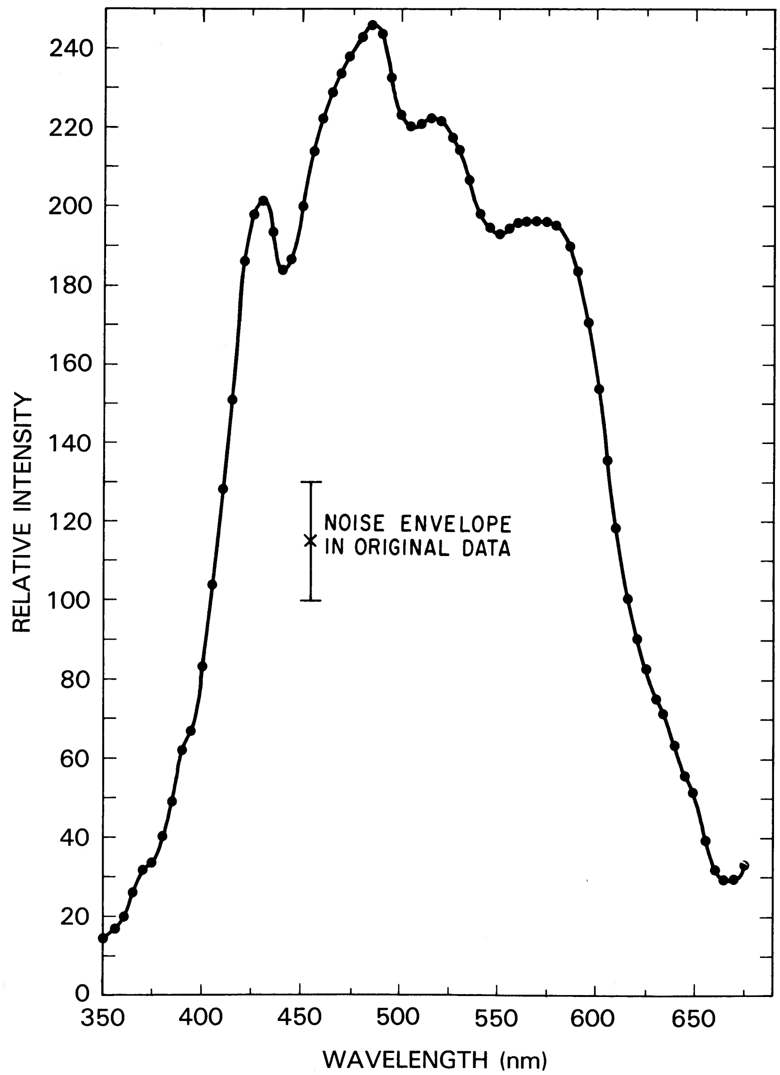

FIG. 2.—Fluorescent spectrum of uniform residue (sample B) excited by 25 nm (FWHM) beam centered at 300 nm

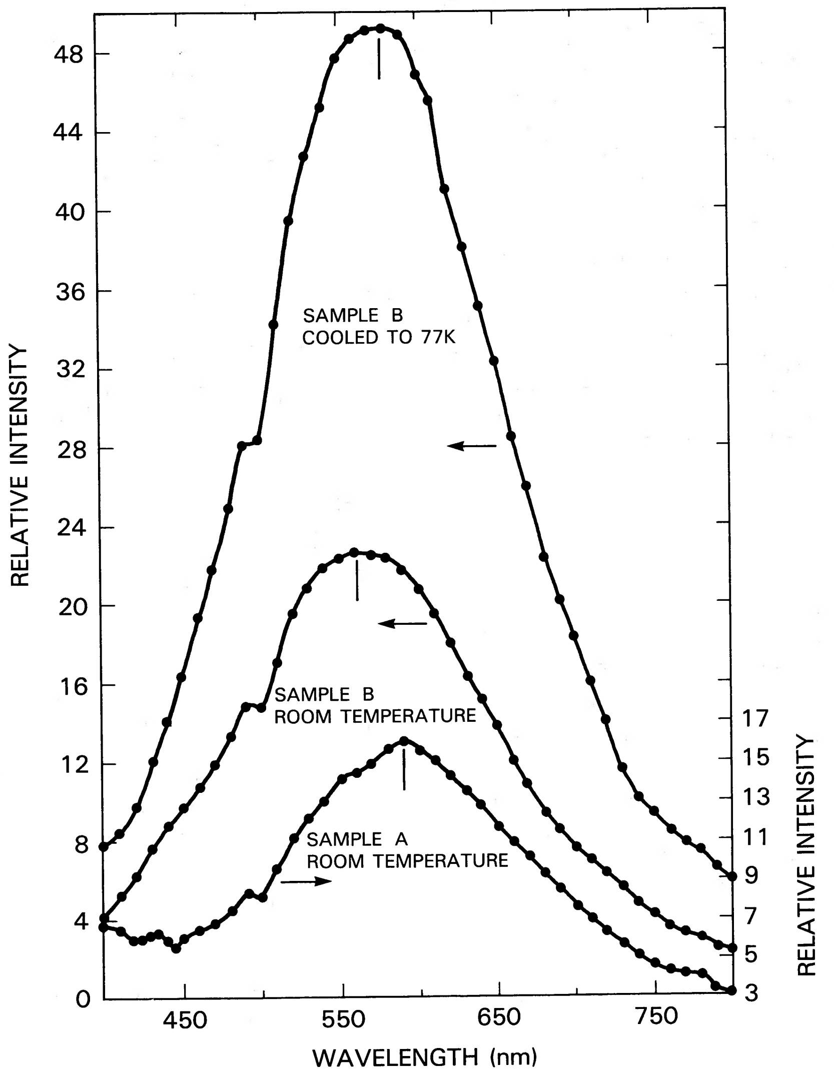

FIG. 3.—Fluorescent spectra of residues excited by 337 nm laser beam. *Upper spectrum:* sample B cooled to liquid nitrogen temperature. *Middle spectrum:* sample B at room temperature. *Lower spectrum:* sample A at room temperature. Intensity scale on left applies to upper two spectra. Right scale is for bottom spectrum.

efficiency is ~40% higher than that of the high argon sample. However, cooling the sample increased the efficiency by nearly a factor of 4. At liquid nitrogen temperature sample D is 2.5 times more efficient than sample C.

IV. DISCUSSION AND CONCLUSIONS

This paper reports the formation and fluorescence of nonvolatile residues from an electrical discharge in a mixture of CO, CH_4, N_2, H_2O, and Ar. The fluorescent spectra are somewhat similar to the broad emission observed in the Red Rectangle. The composition of the mixtures, as discussed in § II, was reasonably consistent with cosmic abundances. This suggests that a complex residue similar to that produced in these experiments could be a constituent of grain mantles in the Red Rectangle and could account for the red emission features. Several questions arise from this simple series of experiments and need to be considered in future work. First, can one reconcile the several hundred angstrom difference between the wavelength region of emission in the Red Rectangle and that of the fluorescence of the samples? Second, how sensitive is the fluorescence to the composition of the initial gas phase and the method of sample preparation? Third, is a mantle similar to the laboratory residue likely to form on grains in dense clouds and, if so, will it be excited to fluoresce?

TABLE 1

QUANTUM EFFICIENCY OF FLUORESCENCE

Sample	Temperature	Q
Riboflavin (standard)	Room temperature	0.25
C	Room temperature	0.05
C	Liquid nitrogen	0.11
D	Room temperature	0.07
D	Liquid nitrogen	0.27

The first two questions are related. The evidence for two slightly different fluorescence spectra for nominally identical samples indicates that the emission depends upon sample characteristics. It further suggests that by varying the methods of preparation a residue can be obtained that will match the Red Rectangle emission feature much more closely than has been done in this work. Such experiments are planned. It is a fair hypothesis that a laboratory attempt to reproduce a complex

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spectrum shows encouraging success if a reasonable sample has a spectrum that is approximately comparable with the observations, and that further work along these lines is warranted.

The last two questions concern the applicability of the laboratory model to the astronomical situation. Infrared and radio observation of HD 44179 and apparently related objects, IRC +10216, and CRL 2688 have found a number of molecules and radicals. In CRL 2688, CO, HCN, HC_3H, and HCO^+ were observed (Zuckerman *et al.* 1976). Molecules identified in IRC +10216 include CO, CH, C_3H, HCN, HC_3N, HC_5N, HC_7N, C_2H, C_2H_2, CH_3CN, CH_4, C_4H, and NH_3 (McCabe, Smith, and Clegg 1980). HD 44179 shows considerable evidence for molecular features in the region between 560 nm and 700 nm (Schmidt, Cohen, and Margon 1980) as well as several very suggestive infrared emission peaks (Russell, Soifer, and Willner 1982). It is consistent with these observations that grains in the Red Rectangle could have as a mantle constituent the type of residue formed in our experiments. The detailed mechanism by which this residue may have formed is left for a later discussion but might involve reactions on grain surfaces induced by ultraviolet irradiation of adsorbed species (Greenberg 1982). Wdowiak (1981) has previously suggested that fluorescent emissions from trapped ions and radicals may explain the sharp emission features in the Red Rectangle. It is necessary to see if both the sharp and broad emission features can be produced in the same sample or if a multiple component system is required.

Duley (1985) has called attention to fluorescence experiments (Watanabe, Hasegawa, and Kurata 1982) on hydrogenated amorphous carbon films. The position of the emission was a function of the deposition temperature. At a temperature of 200° C, the lowest temperature reported, the fluorescent spectrum peaked at ~ 640 nm and was a good match to the smooth background emission of the Red Rectangle. At higher temperatures the emission shifted to longer wavelengths and became double peaked. If the results can be extrapolated to 100 K, the peak would occur at ~ 560 nm. Watanabe *et al.* also found that the fluorescent intensity increased as the measurement temperature was lowered. These results are in good agreement with the measurements of our carbonaceous films.

The optical properties of the particles present in the nebula associated with HD 44179 and similar objects therefore suggest that these particles are a carbonaceous material resulting from the polymerization of a cosmic mixture of the elements. They need not be restricted to simple hydrogenated amorphous carbons as Duley has proposed.

There is an important corollary of several laboratory investigations of the ultraviolet and infrared spectra of carbonaceous films rich in hydrogen. These investigations increasingly suggest that such materials are the source of many observed interstellar and circumstellar features. The major feature in the ultraviolet extinction is the 220 nm bump. Although commonly called the "graphite peak" there are serious problems with that identification, one of which is the unlikely occurrence of interstellar graphite (Cyzsak and Santiago 1973). This is supported by recent measurements on the ultraviolet extinction of the stars R CrB and RY Sgr, variables with a large C/H ratio (Hecht *et al.* 1984). These stars show extinction peaks between 240 nm and 250 nm, characteristic of amorphous carbon. The laboratory measurements on an extinction peak at 2175 nm in the condensate from a discharge in CH_4 may be consistent with grain formation in hydrogen-rich atmospheres or the circumstellar shells of carbon stars. Visible and infrared spectra of frozen products of a gaseous discharge (Wdowiak 1980, 1981) and irradiated ice mixtures (Greenberg, 1982; Moore and Donn 1982) showed encouraging agreement with some diffuse bands and infrared spectral features. Much additional laboratory work is necessary to reproduce and extend the data. Results to date *are supportive* of the hypothesis that grains or mantles primarily of H, C, N, O composition are present in interstellar space and are the source of many of the spectral features observed.

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REFERENCES

Aitken, D. K., Roche, P. F., Spencer, P. M., and Jones, B. 1979, *Astr. Ap.*, **76**, 60.
Black, J. H., and Dalgarno, A. 1977, *Ap. J. Suppl.*, **34**, 405.
Cameron, A. G. W. 1982, in *Essays in Nuclear Astrophysics*, ed. C. A. Barnes, D. D. Clayton, and D. N. Schramm (Cambridge: Cambridge University Press), p. 23.
Czyzak. S. J., and Santiago, J. J. 1973, *J. Ap. Space Sci.*, **23**, 43.
Donn, B., Wdowiak, T., Nuth, J., and Chappelle, E. 1984, *Bull. A.A.S.*, **16**, 462.
Duley, W. W. 1985, *M.N.R.A.S.*, **215**, 259.
Geldzahler, B. J., and Cohen, N. L. 1983, *Pub. A.S.P.*, **95**, 489.
Greenberg, J. M. 1982, in *Comets*, ed. L. Wilkening (Tucson: University of Arizona Press), p. 131.
Greenstein, J. L., and Oke, J. B. 1977, *Pub. A.S.P.*, **89**, 133.
Guelin, M. 1985, in *Molecular Astrophysics*, ed. G. H. F. Diercksen, W. F. Huebner, and P. W. Langhoff (Boston: Reidel), p. 23.
Hecht, J. H., Holm, A. V., Donn, B., and Wu, C. C. 1984, *Ap. J.*, **280**, 228.
Honig, R. E., and Hook, H. O. 1960, *RCA Rev.*, No 1. **21**, (Boca Raton: CRC), p. 360.
McCabe, E. M., Smith, R. C., and Clegg, R. E. S. 1980, in *Interstellar Molecules*, ed. B. H. Andrew (Dordrecht: Reidel), p. 497.
Merrill, K. M. 1979, in *The Interaction of Variable Stars with their Environment*, ed. R. Kippenhahn, J. Rahe, and W. Strohmeier (Bamberg: Remeis-Sternwarte), p. 446.
Moore, M., and Donn, B. 1982, *Ap. J.* (*Letters*), **257**, L47.
Perkins, H. G., Scarratt, S. M., Mardin, P., and Bungham, R. G. 1981, *M.N.R.A.S.*, **196**, 635.
Russell, R. W., Soifer, B. T., and Willner, S. P. 1978, *Ap. J.*, **220**, 568.
Schmidt, G. P., Cohen, M., and Margon, B. 1980, *Ap. J.* (*Letters*), **239**, L133.
Snow, T. P. 1975, *Ap. J.* (*Letters*), **202**, L87.
Thaddeus, P. 1977, in *IAU Symposium 75*, *Star Formation*, ed. T. de Jong and A. Maeder (Boston: Reidel), p. 37.
Warren-Smith, R. R., Scarratt, S. M., and Mardin, P. 1981, *Nature*, **292**, 317.
Watanabe, I., Hasegawa, S., and Kurata, Y. 1982, *Japanese J. Appl. Phys.*, **21**, 856.
Wdowiak, T. J. 1980, *Ap. J.* (*Letters*), **241**, L55.
———. 1981, *Nature*, **293**, 724.
Weast, R. C. 1983, *Handbook of Chemistry and Physics* (63d ed.; Cleveland: CRC).
Webster, A. 1979, *M.N.R.A.S.*, **189**, 33p.
Zuckerman, B., Gilra, D. P., Turner, B. E., Morris, M., and Palmer, P. 1976, *Ap. J.* (*Letters*), **205**, L15.

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