published recently.[7] It was shown that most of the H atoms in this matrix are not trapped in a "spur."[7] Summarizing, we would like to emphasize that the occurrence of a rapid initial period and deviations from simple kinetics for bimolecular reactions in the condensed phase are not sufficient to postulate a nonrandom distribution of the reaction particles. In a forthcoming paper we shall show that this diffusion treatment provides an explanation of the socalled "stepwise" disappearance of trapped radicals in some cases.

(7) J. Zimbrick and L. Kevan, *Nature*, **214**, 693 (1967).

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On the Purported Infrared Absorption at 21 μ of Carbon Monoxide Adsorbed on Silica-Supported Platinum

Sir: The purpose of this letter is to draw attention to the fact that the reported[1] infrared absorption at 476 cm^{-1} of carbon monoxide adsorbed on silica-supported platinum is an artifact. As alluded to in the article by Clarke, *et al.*,[1] the silica disks, even very thin, absorb very strongly in the region 400–1200 cm^{-1}. The 5% transmission at 475 cm^{-1} of the clean disk at room temperature may result from several causes. Apart from such probably dismissory effects as spectrometer stray light or incomplete blocking of the sample beam by the sample disk, the most probable reason for the apparent transmission is the emission of the sample slightly heated above the detector temperature by the undispersed radiation from the spectrometer source. The best confirmation of this mechanism is the apparent increase of transmission when the sample is deliberately heated to 250°. As silica is a strong absorber of radiation of 475 cm^{-1}, it will also be a strong emitter at this frequency. The effects of the apparent transmission change when carbon monoxide is admitted to the sample cell are related to the emissivity of the sample and cannot be directly related to absorption by the Pt–CO groups. Also, the temperature of a sample of small thermal conductivity is itself dependent on its emissivity. The particularly weak nature of the apparent absorption recorded by Clarke, *et al.*,[1] would imply that emission by the supposed Pt–CO groups would also be weak. The breadth of the presumed absorption (about 50 cm^{-1} at half height) provides another clue to the spurious nature of this absorption, as bands observed for carbon monoxide adsorbed on various substrates are generally much narrower. In fact, the 477-cm^{-1} band in the spectrum of Garland, *et al.*,[2] is by Clarke, *et al.*,[1] referred to as being relatively sharp. The large slit width used should still not obscure entirely any fine structure that might be spread over 50 or 70 cm^{-1}. Therefore, any deductions drawn from the position of the spurious 476-cm^{-1} band[1] are unfounded: of course, these criticisms do not specifically apply to spectra of other investigators. Whether or not the purported decrease in transmission[1] is in fact a real decrease in emission due to the adsorbed carbon monoxide remains to be proved by the obtaining of less doubtful spectral changes (*i.e.*, more intense difference spectra) concomitant with admission of carbon monoxide to the sample cell.

The emission from samples in the far-infrared (<700 cm^{-1}) is a common problem in spectroscopy, but one which can frequently be overcome by chopping the radiation between the source and the sample and not between the sample and the detector, as is not the practice in the Grubb–Parsons Spectromaster instrument.[1] A much more likely method of increasing, in some spectral regions, the transmittance of the silica samples would be to cool them near liquid nitrogen temperature.

(1) J. K. Clarke, G. M. Farren, and H. E. Rubalcava, *J. Phys. Chem.*, **72**, 327 (1968).
(2) C. W. Garland, R. C. Lord, and P. F. Troiano, *ibid.*, **69**, 1188 (1965).

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Infrared Absorption at 21 μ of Carbon Monoxide Adsorbed on Silica-Supported Platinum

Sir: Ogilvie[1] is mistaken in contending that we have erred in our interpretation of the 21-μ absorption of carbon monoxide adsorbed on silica-supported platinum.[2] At the outset, the possible artifacts arising from experimental procedures mentioned, *viz.*, stray light or faulty sample placement, can indeed be dismissed; normal precautions were taken to exclude such errors. Further, in recognition of Kirchoff's law, both sample spectra and backgrounds were obtained at the same temperature, which procedure would compensate for temperature-dependent optical effects of the substrate.

Ogilvie correctly states that a strong absorber is a strong emitter. Thus carbon monoxide adsorbed on the platinum would increase the emissivity of the disk in the vicinity of 470 cm^{-1}. If the disk had been

(1) J. F. Ogilvie, *J. Phys. Chem.*, **72**, 2688 (1968).
(2) J. K. A. Clarke, G. M. Farren, and H. E. Rubalcava, *ibid.*, **72**, 327 (1968).