JOURNAL OF CATALYSIS 67, 308–315 (1981)

Dissociation of Alkylamines Adsorbed on Iron and Nickel

R. W. SHEETS[1] AND G. BLYHOLDER

Department of Chemistry, University of Arkansas, Fayetteville, Arkansas 72701

Received April 14, 1980; revised July 24, 1980

Infrared spectra for methylamine, isopropylamine, dimethylamine, and trimethylamine adsorbed on iron and nickel have been obtained. Chemisorption of all four took place at room temperature without noticeable decomposition. When CO is coadsorbed with the amines, the secondary and tertiary amines decompose to give mainly adsorbed primary amine. The results are understandable within the framework of a simple molecular–orbital model of the adsorbed species.

INTRODUCTION

At the heart of heterogeneous catalysis is a knowledge of bond-breaking and bond-forming processes at surfaces. This report focuses on the lability of N–C bonds when the N atom is bonded to a metal surface. We have previously examined the stability of N–H bonds in NH_3 adsorbed on V, Fe, and Ni (*1*). It was found that the nature of the metal and the presence of coadsorbed gases such as CO had a profound effect on the stability of the N–H bond. The question then arises as to the effect of these same factors on the stability of the N–C bond under similar conditions. A practical interest in alkylamines arises because of the use of organic nitrogen bases as selective poisons to improve selectivity in hydrogenation (*2*) and as corrosion inhibitors (*3*).

A general organic text (*4*) states "The cleavage of amines normally requires drastic treatment and is rarely encountered." While this may be a valid statement for homogeneous organic systems, the presence of surfaces creates exceptions. In examining the exchange of deuterium with hydrogen atoms of alkylamines over Fe, Ni, Pt, Pd, and W from −50 to +100°C a self-poisoning effect was observed and ascribed to slow decomposition of the amines on the surfaces (*5*). At elevated temperatures (400 to 600°K) methylamine did not undergo isotopic exchange at the C–N bond over Ni, Pt, Pd, W, Co, V, and Cu but did react with H_2 to produce NH_3 and CH_4 plus a little dimethylamine (*6*). Under these same conditions at elevated temperatures dimethylamine (DMA) reacted with H_2 to disproportionate to methylamine (MA) plus trimethylamine (TMA) and to hydrogenate to NH_3 plus CH_4. On the basis of deuterium exchange not occurring, the adsorption of *n*-butylamine and *n*-hexylamine on reduced iron powder was concluded to be nondissociative (*3, 7*). These studies indicate that metal surfaces do have a substantial effect on the stability of N–C bonds.

Infrared spectroscopy provides a means of determining the structure of molecules while they are on the surface. Infrared spectra of MA, DMA, and TMA adsorbed on Zn(II) and Co(II) halides gave no indication of dissociation for the adsorbed amines (*8*). While infrared spectra indicate undissociated NH_3 adsorption on V and Fe, the fact that addition of CO results in formation of a small amount of surface isocyanate (–NCO) indicates that a small fraction of the NH_3 does dissociate on V and Fe surfaces (*9*). The formation of isocyanate at room temperature suggests that the activation energy for formation of the N–C bond is not very large. To further examine the stability of N–C bonds at room temperature, the

---

[1] Present address: Department of Chemistry, Southwest Missouri State University, Springfield, Mo. 65802.

0021-9517/81/020308-08$02.00/0

surface structures resulting from exposure of alkylamines to Fe and Ni surfaces were determined.

EXPERIMENTAL

The wide spectral range experimental technique, which has been described in detail elsewhere (*10*), consists of evaporating a metal from an electrically heated tungsten filament in the presence of a small pressure of helium. The metal particles formed in the gas phase deposit on a hydrocarbon oil film on the salt windows of an infrared cell. Metal particles formed in the gas phase have been shown to form regular crystallites with a diameter size distribution centered in the range 50 to 200 Å (*11–13*). These dispersed particles are referred to hereafter as films both for convenience and because it is believed that their behavior is similar to that of vacuum-evaporated films. The gas to be studied is then admitted to the cell, and the spectrum of the chemisorbed species obtained. Spectra are recorded before and after admission of the gas to the cell. Five minutes of pumping has been found sufficient to remove all spectra due to gas-phase molecules. The 25°C temperature listed for measurements is an average, as all measurements were taken at room temperature.

The spectra were obtained using a Perkin–Elmer Model 337 spectrophotometer. This is a grating instrument which scans the region 4000–400 cm^{-1}. No unusual spectrometer settings were used.

The adsorbates were obtained as reagent-grade chemicals from commercial sources. They were degassed by repeated freeze–thaw cycles in the vacuum system. The CO was passed through an activated-charcoal trap cooled with liquid air.

This technique has the advantage that a wide infrared spectral region is available for study. It has the disadvantage that the metal surface is covered with oil. This oil is apparently only weakly adsorbed since many gases have been found to chemisorb readily on the metal. Essentially, the oil is regarded as a solvent which has weak interactions with the systems of interest. Having a wide spectral range available aids greatly in attempts to determine structure. The skeletal vibrations in the region 1300 to 700 cm^{-1} are necessary for determining the structure of the adsorbed alkylamines but are obscured by SiO_2 or Al_2O_3 vibrations if silica or alumina is used as support material. It has been shown that there are no fundamental differences between alcohols, aldehydes, and ketones adsorbed on silica-supported Fe, Co, or Ni (*14*) and alcohols, aldehydes, and ketones adsorbed on Fe, Co, and Ni crystallites in a hydrocarbon matrix produced by the method used here (*15–17*).

RESULTS

Evaporated nickel and iron films were exposed to MA at a pressure of 30 Torr for 1 hr. These films were subsequently exposed to a 30-Torr pressure of CO for 30 min. The spectra for nickel are shown in Fig. 1 and the observed bands and assignments for both nickel and iron are listed in Table 1. The spectra for iron are similar to those for nickel and so are not shown.

The spectra resulting from a 30-Torr pressure of isopropylamine over a nickel film for 4 hr followed by a 30-Torr pressure of CO for 30 min are shown in Fig. 2. The infrared bands and their assignments are given in Table 2 together with the results for a similar experiment with Fe. Since the spectra for iron are similar to those for nickel, they are not shown.

DMA at a pressure of 30 Torr when placed over nickel or iron produces the bands listed in Table 3 and spectra like those in Fig. 3. The changes produced by adding 30 Torr of CO for 30 min are also given. The iron spectra are not shown because they are similar to the nickel spectra.

The adsorption of TMA on Ni and Fe films was quite slow. The spectra obtained after a 15-hr exposure at 60-Torr pressure over Ni and the effect produced by 30 Torr of CO for 30 min are shown in Fig. 4.

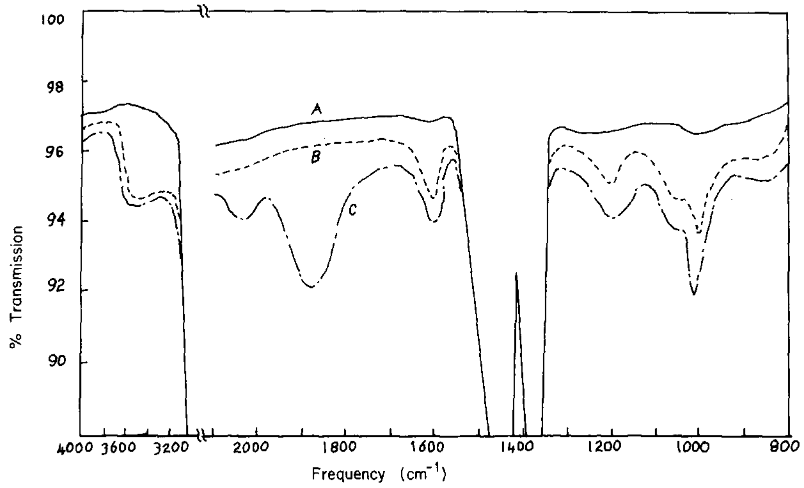

FIG. 1. Infrared spectram (cm^{-1}) of methylamine and CO adsorbed on nickel. (A) Background; (B) chemisorbed methylamine; (C) CO added to (B).

Similar spectra for Fe were obtained, but are not shown. Table 4 lists the band positions and their assignments for both Fe and Ni. If the films were exposed first to CO and then to DMA at a pressure of 50 Torr for 4 hr, the results were the same except that the infrared bands were larger.

DISCUSSION

Methylamine chemisorbed readily on iron and nickel, producing bands of moderate intensity (Fig. 1). The spectra for the two metals were nearly identical (Table 1). The similarities between the spectrum of

TABLE 1

Frequencies (cm^{-1}) and Band Assignments for Methylamine and Carbon Monoxide on Iron and Nickel at 25°C

MA (*18*) vapor	MA on nickel	MA and CO on nickel	MA on iron	MA and CO on iron	Assignment
3387 3360	3250	3250	3300	3300	N–H stretch
2962 2842 2822		Region obscured by background oil bands			C–H stretch
1622	1600	1600	1590	1590	NH_2 bend
1460 1410		Obscured by oil			CH_3 bend
1244 1129	1200	1200	1190	1190	CH_3 rock
1044	1045 1000	1045 1010	1040 975	1040 980	C–N stretch
779	815	815	810	810	NH_2 rock
		2030 1890		1920 580	Added CO

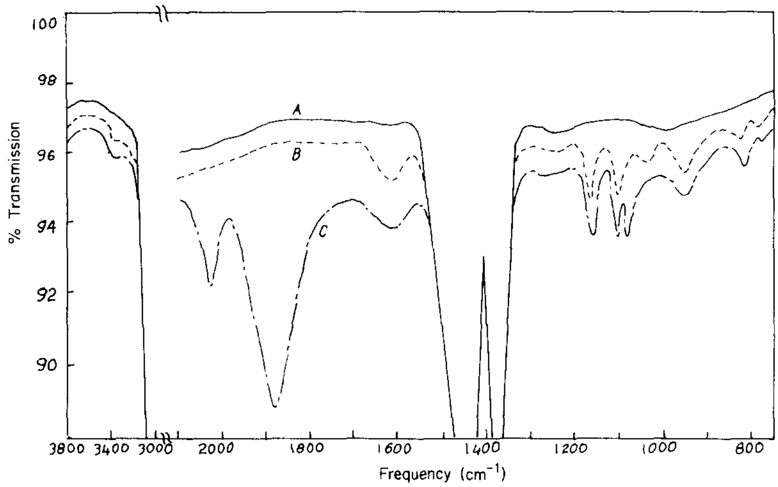

FIG. 2. Infrared spectra (cm^{-1}) of isopropylamine and CO on nickel. (A) Background; (B) chemisorbed isopropylamine; (C) CO added to (B).

TABLE 2

Frequencies (cm^{-1}) and Band Assignments for Isopropylamine (IPA) and Carbon Monoxide on Nickel and Iron at 25°C

IPA (*19, 20*) vapor	IPA on nickel	IPA and CO on nickel	IPA on iron	IPA and CO on iron	Assignment
3430 3330	3300	3300	—	3350	N—H stretch
2980 2880		Region obscured by background oil bands			C—H stretch
1630	1600	1600	1610	1610	NH_2 bend
1470		Obscured by oil			CH_3 bend
1390 1380		Obscured by oil			$C(CH_3)_2$
1350		Obscured by oil			C—H bend
1170	1165	1165	1160	1160	C C—N skeletal C
1130	1105	1105	1110	1110	
1040	1030	1080	1030	1060	C—N stretch
980	940	940	940	940	
825	810	810	810	810	NH_2 rock
785	785	785	775	775	
		2030 1890		1920	Added CO

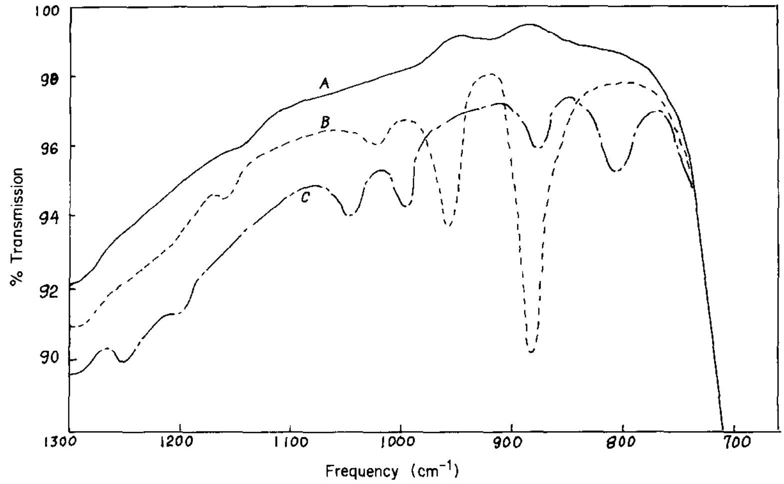

FIG. 3. Infrared spectra (cm^{-1}) of dimethylamine and CO on nickel. (A) Background; (B) chemisorbed dimethylamine; (C) CO added to (B).

MA vapor and the spectra of chemisorbed MA suggest that chemisorption has occurred without dissociation, probably through donation of the lone-pair electrons on the nitrogen atom to the metal surface. Similar conclusions were reached by Yao (*3*, *7*) in his studies of alkylamines chemisorbed on iron powders at 25°C in which adsorption was measured by using continuous-flowing gas mass spectrometry. Only one band was observed in the N–H stretching region, 3500–3200 cm^{-1}. Resolution in this region was poor, however, and the band is broad enough to contain both the asymmetric and the symmetric stretching bands. Furthermore, the bands near 1600 and 800 cm^{-1} are in the correct regions for NH_2 groups (*19*).

Subsequent chemisorption of CO on these films had little effect on the MA spectra. The band at 1000 cm^{-1} on nickel and at 975 cm^{-1} on iron, which was tentatively assigned to the C–N stretching vibration, was shifted 10–15 wavenumbers to a higher frequency. No other band was shifted. In some of the runs, the intensities

TABLE 3

Frequencies (cm^{-1}) and Band Assignments for DMA and CO on Ni and Fe at 25°C

DMA (*21*) vapor	DMA on nickel	DMA on iron	DMA and CO on nickel	DMA and CO on iron	MA on nickel	Assignment
			1255	1255	1250sh	CH_3 rock
1245			1200	1200	1200	CH_3 rock
1155	1160	1150				
1078						
1024	1020	1020	1045	1040	1045	C–N stretch
			1000	990	1000	
930	960	960				
724	890	890				N–H bend
			815	810	815	NH_2 rock
			2030	1920		Added CO
			1890			Added CO

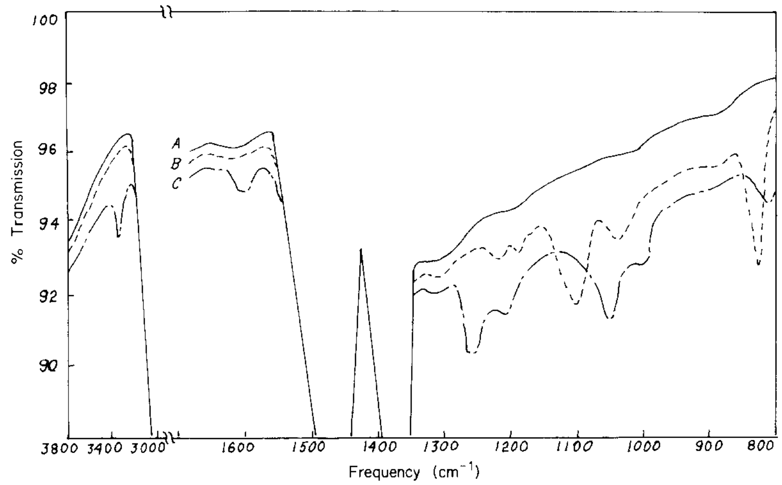

FIG. 4. Infrared spectra (cm^{-1}) of trimethylamine and CO on nickel. (A) Background; (B) chemisorbed trimethylamine; (C) CO added to B.

of the C–N bands were increased a few percent on addition of CO. No increase in CH_3 band intensities was observed. It therefore seems that the increased intensities are due to changes in the extinction coefficients of these bands. The subsequent adsorption of CO has apparently changed the electronic structure of the surface and thereby affected the dipole moment change and the band intensity. The CO bands themselves were shifted to lower frequencies, as was the case for ammonia and CO, indicating that electrons are being donated to the surface by the amine.

Isopropylamine was chemisorbed without difficulty on both iron and nickel films (Fig. 2). Since no complete vibrational analysis for IPA is available, some of the assignments in Table 2 are tentative. Comparison of the spectra of the vapor and chemisorbed states, however, again indicates that no dissociation has occurred. As in the case of MA, subsequent chemisorption of CO tended to cause an increase in the band intensity and a shift to higher frequency of the C–N stretching band. No decomposition of the chemisorbed species was noted.

TABLE 4

Frequencies (cm^{-1}) and Band Assignments for TMA and CO on Nickel and Iron at 25°C

TMA (*22*) vapor	TMA on nickel	TMA on iron	TMA and CO on nickel	TMA and CO on iron	MA on nickel	Assignment
			3350	3100	3250	N–H stretch
			1600	1590	1600	NH_2 bend
			1255		1250sh	CH_3 rock
1273	1210	1210	1200	1190	1200	CH_3 rock
1183	1190	1180				
1102	1115	1100				
1043	1040	1030	1045	1040	1045	C–N stretch
			1000	990	1000	
825	825	820				
			815	810	815	NH_2 rock
			2030	1920		Added CO
			1890			Added CO

Chemisorption of DMA was accomplished by exposure of iron and nickel films for several hours. The chemisorbed band assignments in Table 3 were made by comparison with the spectra of DMA in the vapor and solid states (*21*).

The band occurring at 880–890 cm^{-1} in spectra of chemisorbed DMA is especially interesting. Finch and co-workers (*21*) report that the N–H bending vibration which occurs at 724 cm^{-1} in the vapor is shifted to 882 cm^{-1} in the solid because of hydrogen bonding in the solid. Spectra of chemisorbed DMA do not have any bands in the 700-cm^{-1} region. For all of the metals studied, however, there is a band near 890 cm^{-1} which has no counterpart in the vapor spectrum. Assigning this band by analogy to the solid-state DMA spectrum gives a N–H shift indicative of a strong interaction between the hydrogen atom on the nitrogen and a third atom, probably a metal surface atom.

When CO is subsequently chemisorbed on iron and nickel films containing preadsorbed DMA, the spectra are completely changed as Fig. 3 shows. The appearance of the new bands and the disappearance of the original bands are indicative of drastic restructuring of the surface species. When decomposition of DMA occurs, it seems likely that a variety of species are produced. In a mass spectrometric study of the reactions of aliphatic amines over evaporated metal films at elevated temperatures, Anderson and Clark (*6*) found that on palladium and nickel, DMA was converted to mainly monomethyl- and trimethylamine. In the present study, the spectrum of DMA chemisorbed simultaneously with CO at room temperature in Table 3 shows a close correspondence to the spectra of chemisorbed methylamine. This indicates that MA is one of the main species formed when CO is added to DMA chemisorbed on iron and nickel.

It was necessary to expose metal films to TMA for periods of up to 15 hr in order to obtain useful spectra. On iron and nickel, TMA appeared to chemisorb without dissociation. Table 4 shows the similarities between TMA vapor and TMA chemisorbed on iron and nickel. Furthermore, infrared spectra of charge-transfer complexes of TMA, such as $(CH_3)_3N \cdot I_2$ (*23*), are also very similar to those of chemisorbed TMA, adding support to the suggestion that TMA chemisorbs without dissociation via coordination of the nitrogen atom to a surface metal atom.

Exposure of iron and nickel films containing preadsorbed TMA to CO resulted in the chemisorption of CO and a rapid decomposition of the TMA surface species as indicated by the spectra in Fig. 4 and the comparisons in Table 4. The resulting spectra were like those of DMA chemisorbed simultaneously with CO, that is, they resembled spectra of chemisorbed MA, although more complex. No bands attributable to undissociated chemisorbed DMA were detected. When iron and nickel films were exposed first to CO and then to TMA, only spectra resembling dissociated DMA surface species were obtained.

Again the work of Anderson and Clark (*6*) is pertinent. They found that for the reaction of TMA over palladium at 170–280°C, the major products were DMA and MA. It appears that a similar decomposition takes place when TMA is chemisorbed on iron and nickel along with CO at room temperature. Just as in the case with adsorbed NH_3 (*1*), this again demonstrates that a coadsorbed gas may radically affect the stability and structure of the other adsorbate.

In comparing the adsorption behavior of NH_3 and the alkylamines on Ni, NH_3 adsorbs readily and with dissociation (*1*), MA and DMA adsorb readily but without dissociation, while TMA adsorbs quite slowly without dissociation. Thus the N–C bond is les labile than the N–H bond when the N atom is coordinated to Ni atoms on the surface. This behavior also shows that when the adsorbed nitrogen maintains at least one stable bond to a nonsurface atom, the hydrogen atoms are more stable bonded to the nitrogen than migrating onto the surface metal atoms. The slower adsorption of TMA than MA and DMA may be ascribed to hydrogen bonding contributing to the stability of adsorbed MA and DMA but not to the stability of adsorbed TMA. The occurrence of hydrogen bonding by DMA to the surface as shown by the N–H bending frequency shift has already been discussed. TMA has no nitrogen-bonded hydrogen atoms to form hydrogen bonds. In Table 1 the N–H stretching frequency of adsorbed MA is seen to be shifted over 100 cm^{-1} to lower frequencies than occur in gas-phase MA, thus indicating hydrogen bonding to the surface.

The large effect of coadsorbed CO on the stability of the adsorbed alkylamines may be rationalized in terms of a simple molecular–orbital model for the adsorbed species. In this model (*24, 25*) the π^* orbitals of chemisorbed CO can accept electrons from the surface with a consequent shift of the chemisorbed CO stretching frequency to lower values. That CO is removing electrons from the surface is shown by the CO stretching frequencies given in Tables 1 to 4 being considerably downshifted from the values for CO alone on Fe at 1950 cm^{-1} and on Ni at 2060 and 1920 cm^{-1} (*25*). When CO is coadsorbed with DMA and TMA this effect results in the metal atom to which the nitrogen is coordinated becoming more positive than it is in the absence of the CO and methyl migrations to positive centers are well known. Thus the decomposition of DMA and TMA in the presence of chemisorbed CO becomes understandable. Apparently the presence of a nonmigrating alkyl group also helps to reduce the energy of the transition state since adsorbed MA is found to be stable in the presence of chemisorbed CO.

In summary, chemisorption of all four amines took place without noticeable decomposition. When simultaneously chemisorbed with CO the secondary and tertiary amines decomposed to give mainly a primary amine. These results are understandable within the framework of a simple molecular–orbital model for the adsorbed species.

REFERENCES

1. Blyholder, G., and Sheets, R., *J. Catal.* **27**, 301 (1972).

2. Bond, G. C., "Catalysis by Metals," pp. 296–297. Academic Press, New York, 1962.

3. Yao, Y., *J. Phys. Chem.* **67**, 2055 (1963).

4. Fuson, R. C., "Advanced Organic Chemistry," p. 533. Wiley, New York, 1950.

5. Kemball, C., and Wolf, F. J., *Trans. Faraday Soc.* **51**, 1111 (1955).

6. Anderson, J. R., and Clark, N. J., *J. Catal.* **5**, 250 (1966).

7. Yao, Y., *J. Phys. Chem.* **68**, 101 (1964).

8. Guilbault, G. G., and Billedeau, S. M., *J. Inorg. Nucl. Chem.* **34**, 1167 (1972).

9. Sheets, R., and Blyholder, G., *J. Phys. Chem.* **79**, 1572 (1975).

10. Sheets, R., and Blyholder, G. *Appl. Spectrosc.* **30**, 602 (1976).

11. Hill, P. H., and Turkevich, J., U.S. Atomic Energy Commission Report NYO-3435, 1956.

12. Kimoto, K., Kamiya, Y., Nonoyama, M., and Uyeda, R., *Japan. J. Appl. Phys.* **2**, 702 (1963).

13. Kimoto, K., and Nishida, I., *Japan. J. Appl. Phys.* **6**, 1047 (1967).

14. Blyholder, G., and Wyatt, W. V., *J. Phys. Chem.* **70**, 1745 (1966).

15. Blyholder, G., and Neff, L. D., *J. Phys. Chem.* **70**, 893 (1966).

16. Blyholder, G., and Neff, L. D., *J. Phys. Chem.* **73**, 3494 (1969).

17. Blyholder, G., and Neff, L. D., *J. Phys. Chem.* **70**, 1738 (1966).

18. Barcelo, J., and Bellanato, J., *Spectrochim. Acta* **8**, 27 (1956).

19. Stewart, J. E., *J. Chem. Phys.* **30**, 1259 (1959).

20. Coltkup, N., Daly, L., and Wiberly, S., "Introduction to Infrared and Raman Spectroscopy," p. 386. Academic Press, New York, 1964.

21. Finch, A., Hyams, I., and Steele, D., *J. Mol. Spectrosc.* **16**, 103 (1965).

22. Gayles, J. N., *Spectrochim. Acta* **23A**, 1521 (1967).

23. Yobayashi, K., Watari, F., and Aida, K., *Spectrochim. Acta* **24A**, 1651 (1968).

24. Blyholder, G., *J. Phys. Chem.* **68**, 2772 (1964).

25. Blyholder, G., and Allen, M., *J. Amer. Chem. Soc.* **91**, 3158 (1969).