J. Am. Chem. Soc. 1986, 108, 5827-5830

Cation Binding at the Air-Water Interface by Macromolecules Bearing Pendant Crown Ether Moieties

Jeffrey M. Gold,[†] David M. Teegarden,[‡] Kathleen M. McGrane, David J. Luca, Pasquale A. Falcigno,[†] Cindy C. Chen, and Thomas W. Smith[*]

Contribution from the Xerox Corporation, Webster Research Center, Webster, New York 14580.

Received December 9, 1985

Abstract: In solution, the ion-binding characteristics of crown ethers and macromolecules containing macrocyclic ether moieties have been studied extensively. These ionophores are finding application in membranes, thin film sensors, and ion-selective electrodes. In these devices, interfacial binding equilibria are most pertinent. This paper presents the results of a detailed analysis of the pressure vs. area behavior of Langmuir films of poly(4′-vinylbenzo-18-crown-6), P18C6, spread on pure water and aqueous solutions of alkali metal salts. Our results show that the compression isotherms can be quantitatively related to the nature of the cation in the subphase and its concentration. At the air-water interface, the polymer is in a highly extended conformation and cooperative binding between proximate crown ether groups is precluded. Accordingly, the affinity of the polymer for Li$^+$, Na$^+$, K$^+$, Rb$^+$, and Cs$^+$ at the air-solution interface mirrors that of the monomeric analogue, benzo-18-crown-6, in solution and is inverse to that of P18C6 in solution. Equilibrium binding constants for complexation of P18C6 to K$^+$ at the air-water interface are comparable to those for binding of P18C6 to K$^+$ in aqueous solution.

In the past decade, the binding of ions by macrocyclic polyethers has been a subject of intense interest with studies of the relationship between structure and binding being most prevalent.[1-4] Smid et al. have demonstrated that macromolecules bearing macrocyclic ether pendant groups strongly bind ions of different size, including ions whose ionic radii exceed the size of the polyether cavity.[5,6] The differences in the binding characteristics of poly(vinyl macrocylic polyethers) and their monomeric analogues arise from the possibility of cooperative binding between proximate crown residues on the polymer chain. Ionophoric polymers of this type are being examined in thin film sensors,[7] transducers,[8] ion-exchange membranes,[9,10] and ion-selective electrodes[11] and as solid electrolytes[12] Their utility in these systems is a function of their interfacial binding characteristics.

This paper presents the results of a detailed study of the alkali metal cation binding characteristics of a monolayer of macromolecules with pendant crown ether groups. The pressure area, π vs. A, behavior of polymers which spread at the air-water interface is described in the early work of Crisp.[13] Ter-Minassian-Saraga et al. have described the monolayer characteristics of polyacids[14] and polysoaps[15] and the effect of counterion binding on monolayer characteristics in these systems. The π vs. A behavior of nonionic polymers spread on an aqueous subphase containing specific metal ions, however, has only recently received attention.[16] Poly(4′-vinylbenzo-18-crown-6), P18C6, was chosen for our monolayer experiments because certain features of its binding of alkali metal cations, in solution, have been described in the literature.[5,6,17,18] The present studies were carried out in Langmuir films at the air-water interface by spreading P18C6 on pure water and on 0.1 M solutions of alkali metal chlorides (LiCl, NaCl, RbCl, and CsCl). Compression isotherms were also determined on aqueous solutions of KCl as a function of salt concentration in the range 0.01-1.0 M. In parallel with this work, extensive studies of the binding of ions to P18C6 in homogeneous solutions have been carried out. While information pertinent to this discussion will be presented here, the study of binding in homogeneous solution will be reported separately.[19]

Experimental Section

P18C6 was synthesized from its monomeric precursor, (4′-vinylbenzo-18-crown-6),[5] by standard free-radical polymerization techniques (sealed glass ampoules, benzene, azobisisobutyronitrile). The resulting polymer had an intrinsic viscosity of 0.25 dL/g in benzene at 25 °C. Size exclusion chromatography gave styrene equivalent molecular weights: M_w = 39 900; M_n = 30 900; polydispersity = 1.29 (solvent: DMF, columns: three ASI m Styragel-linear mixed bed, ASI Analytical Services, Santa Clara, CA).

Table I. Extraction of Metal Picrate Salts by Crown Ethers[a]

M$^+$	% M$^+$ picrate extracted by	
	18-crown-6	P18C6
Li	8.4	9.5
Na	19	29
K	93	90
Rb	90	93
Cs	71	100

[a] See text for experimental conditions.

Extraction experiments were carried out at 25 ± 0.5 °C in a fashion similar to that described by others[1,5] using an aqueous phase containing 0.1 M M$^+$OH$^-$ (M = Li, Na, K, Rb, Cs) with 5.7 × 10^{-5} M picric acid and an organic phase of methylene chloride with 2.85 × 10^{-4} M crown ether units. Percent picrate salt extracted into the organic phase was

---

[*] To whom correspondence should be addressed.

[†] Present address: Department of Chemistry, University of Rochester, Rochester, NY 14627.

[‡] Present Address: St. John Fisher College, Rochester, NY 14618.

(1) Pedersen, C. J.; Frensdorff, H. K. *Angew. Chem., Int. Ed. Engl.*, **1972**, *11*, 16-25.

(2) Lehn, J.-M. *Acc. Chem. Res.* **1978**, *11*, 49.

(3) Gokel, G. W.; Goli, D. M.; Minganti, C.; Echegayen, L. *J. Am. Chem. Soc.* **1983**, *105*, 6786.

(4) Takeda, V. "The Solvent Extraction of Metal Ions by Crown Compounds" In *Topics in Current Chemistry, Host Guest Complex Chemistry III*, Vögtle, F., Weber, E., Eds.; Springer-Verlag: Berlin, 1984.

(5) Kopolow, S.; HogenEsch, T. E.; Smid, J. *Macromolecules* **1973**, *6*, 133-142.

(6) Shah, S.; Kopolow, S.; Smid, J. *J. Polym. Sci., Polym. Chem. Ed.*, **1976**, *14*, 2023.

(7) Huang, Q.; Fang, P. *Huaxue Xuebao*, **1984**, *42*, 189; *Chem. Abstr.* **1984**, *100*, 105192m.

(8) Shinkai, S.; Manabe, O. "Photocontrol of Ion Extraction and Ion Transport by Photofunctional Crown Ethers," in ref. 4.

(9) Blasius, E.; Janzen, K. P. *Top. Curr. Chem.* **1981**, *98*, 165.

(10) Wong, K. H.; Yagi, K.; Smid, J. *J. Membr. Biol.* **1974**, *18*, 379.

(11) Morf, W. E.; Simon, W. In *Ion-Selective Electrodes in Analytical Chemistry*; Freiser, H., Ed.; Plenum: New York, 1980; Vol. 1.

(12) Shriver, D. F.; Papke, B. L.; Ratner, M. A.; Dupon, R.; Wong, T.; Brodwin, M. *Solid State Ionics* **1981**, *5*, 83.

(13) Crisp, D. J. In *Surface Phenomena in Chemistry and Biology* Danielli, J. F., Pankhurst, K. G. A., Riddiford, A. C., Eds.; Pergamon Press: New York, 1958; pp 23-54.

(14) Ter-Minassian-Saraga, L.; Abitboul, S. J. *J. Colloid Interface Sci.* **1974**, *48*, 32. Ter-Minassian-Saraga, L.; Thomas, C., *Ibid.* **1974**, *48*.

(15) Ter-Minassian-Saraga, L.; Plaisance, M. *J. Colloid Interface Sci.* **1976**, *56*, 33; **1977**, *59*, 113.

(16) Eley, D. D.; Hey, M. J.; Speight, J. M. *J. Chem. Soc., Faraday Trans. 1* **1983**, *79*, 755-763.

(17) Varma, A. J.; Smid, J. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1189.

(18) Wong, L.-H.; Smid, J. *Polymer* **1980**, *21*, 195.

(19) Smith, T. W.; Chen, C. C. *J. Polym. Sci., Polym. Symp.* **1986**, *74*, 171-185.

0002-7863/86/1508-5827$01.50/0

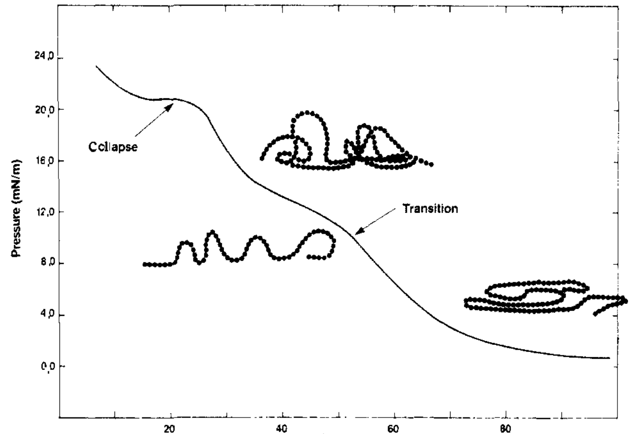

Figure 1. Compression isotherm (20 °C) for P18C6 spread on pure water. Film was spread at 200 Å²/residue and compressed at a rate of 13 Å²/(residue·min).

determined spectrophotometrically.

Monolayer films of P18C6 were spread at 20.0 ± 0.1 °C from chloroform solution [0.2 mg/mL, $CHCl_3$, MCB Omnisolv (stabilized with pentene) redistilled from K_2CO_3 under an N_2 atmosphere and stored in the dark] onto an aqueous subphase in a Lauda film balance equipped with a solid Teflon trough. Salts added to the subphase were LiCl, NaCl, KCl (Baker); and RbCl and CsCl (Alfa, ultrapure). Water purification and other experimental procedures were essentially the same as those used by Arnett et al.[20] Films of P18C6 on water or salt solution are stable and the compression isotherms are reversible, provided the film is not compressed beyond the equilibrium collapse pressure. If compressed to such an extent, the π vs. A isotherms exhibit marked hysteresis.

Results and Discussion

In picrate extraction experiments, P18C6 binds alkali metal cations in the order $Cs^+ > Rb^+ > K^+ \gg Na^+ > Li^+$. This ordering differs from that of monomeric 18-crown-6. Table I presents the data which we have taken for extraction of aqueous metal picrate salts into methylene chloride containing P18C6 or 18-crown-6. The monomeric crown extracts relatively small amounts of the Li^+ and Na^+ picrate salts and a maximum of 93% extraction of K^+ picrate. Percent extraction of Rb^+ and Cs^+ picrates are lower than that for the potassium salt. In contrast, P18C6 extracts Rb^+ and Cs^+ picrates even more efficiently than it does K^+ picrate, reaching 100% extraction of Cs^+ picrate. This is presumably because the polymer's crown ether pendant groups can form 2:1, crown to cation, "sandwich" complexes in addition to the 1:1 complexes formed by isolated crown units. These results are similar to those reported by other workers who have studied the binding characteristics of polymers bearing pendant crown ether groups.[1,5,21,22]

Compression isotherms for P18C6 spread on pure water solutions are shown in Figure 1. The behavior of polymer films at the air–water interface differs markedly from that of long-chain surfactants (e.g., stearic acid). Surfactants bearing one polar headgroup and one or two long hydrocarbon tails orient when compressed to form structures resembling two-dimensional crystals which can support relatively high surface pressures ($\pi > 30$ mN/m). On pure water P18C6 spreads to form an expanded film with π vs. A behavior similar to that described by Crisp[13] for polar polymers which spread to form monolayers at the air–water interface. The isotherm exhibits two transitions, one at about 40 Å²/residue and one at 20 Å²/residue. As the polymer film is compressed, the surface pressure rises to ~12 mN/m at about 40 Å²/residue, goes through an inflection, rises again, and at 20 Å²/residue the surface pressure plateaus at ~21 mN/m. This final plateau occurs at the equilibrium collapse pressure of the film, i.e., the surface pressure at which the film is in equilibrium with the subsurface bulk phase.[23] In the region of the isotherm where the surface pressure is rising nearly linearly (A = 70–40 Å²), the pressure is due to repulsion between macromolecules. We postulate that the inflection arises from conformational transitions wherein the highly expanded macromolecule becomes more compact as pendant crown moieties are forced off the water surface. Long-chain α,ω hydroxy acids are bifunctional surface active molecules which exhibit similar inflections upon compression. The conformation of the molecule is initially bent, as in a hairpin, with both hydroxyl and carboxyl ends at the interface. Upon compression, the more weakly bound hydroxyl group is removed from the surface and a close packed array of fully extended molecules is formed.[24] Isotherms for P18C6 on pure water and on 0.1 M LiCl are similar (see Figure 2); this might be expected since Li^+ does not bind strongly to the 18-crown-6 cavity.

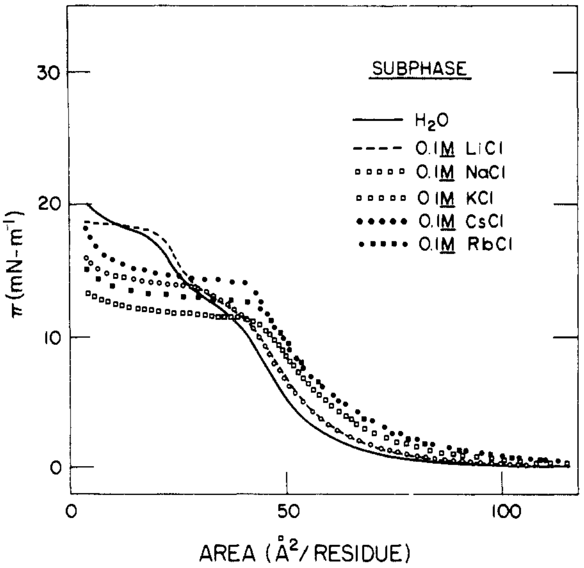

Figure 2. Compression isotherms (20 °C) for P18C6 spread on pure water ( ) and subphases containing 0.1 M M^+Cl^- (M = Li (---), Na (○ ○ ○), K (□ □ □), Rb (■ ■ ■) and Cs (● ● ●)). Films were spread at 200 Å²/residue and compressed at a rate of 13 Å²/(residue·min).

Table II. Pressure and Area of Plateau Onset during Compression of Poly(4′-vinylbenzo-18-crown-6) Monolayers Spread on 0.1 M M^+Cl^- Solutions (T = 20 °C, pH 5.6–5.8)

M^+	π (mN·m⁻¹)	A (Å²/residue)
none	17.5	20.0
Li	18.0	20.5
Na	13.7	37.0
K	11.4	43.5
Rb	13.0	43.0
Cs	14.3	42.0

When larger alkali metal cations (Na^+, K^+, Rb^+, Cs^+) are added to the subphase, profound changes in the π vs. A behavior of P18C6 are observed. These compression isotherms show a single transition at the equilibrium collapse pressure of the film.

The order of the collapse pressure of the films ($Li^+ \gg Na^+ \sim Cs^+ > Rb^+ > K^+$) is reminiscent of the sequence observed in the binding of alkali metal ions to 18-crown-6 and is suggestive of a correlation between the ion-binding properties of P18C6 as determined by extraction (Table I) and the equilibrium collapse pressure of the film. Table II summarizes the collapse pressure and area data. When a cation is complexed with the crown ether ring the polymer becomes more water soluble. Given that this is the case, it would be expected that the surface pressure at which

---

(20) (a) Arnett, E. M.; Chao, J.; Kinzig, B. J.; Stewart, M. V.; Thompson, O.; Verbiar, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 389–400. (b) Arnett, E. M.; Gold, J. M. *Ibid.* **1982**, *104*, 636–639.

(21) Yagi, K.; Ruiz, J. A., Sanchez, M.; *Makromol. Chem., Rapid Commun.* **1980**, *1*, 263.

(22) Kimura, K.; Maeda, T.; Shono, T. *Talanta* **1979**, *26*, 945.

(23) Gaines, G. L., Jr. *Insoluble Monolayers at Liquid/Gas Interfaces*; Interscience: New York, 1966; pp 281–300.

(24) Kellner, B. M. J.; Cadenhead, D. A., *J. Colloid Interface Sci.* **1978**, *63*, 452.

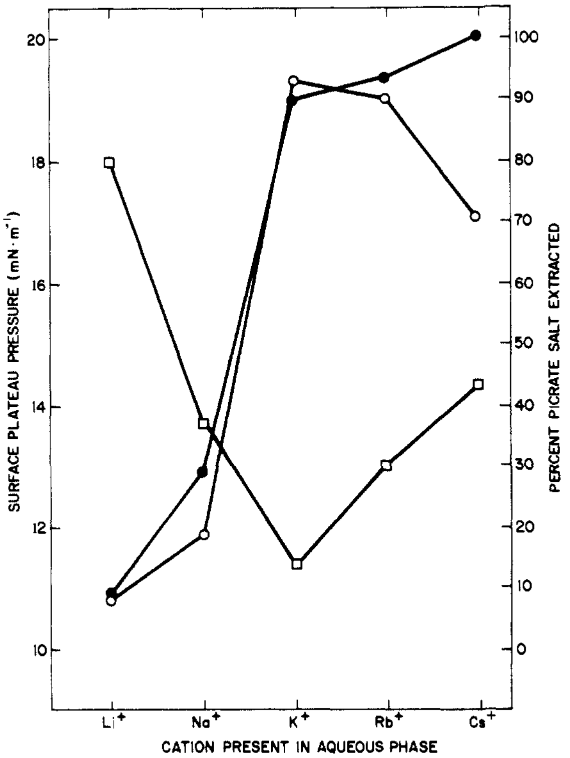

Figure 3. Alkali metal cation binding behavior of P18C6 in solution (●) as a function of percent metal picrate extracted (see text) and at the air–water interface (□) as a function of the surface pressure at which the plateau region begins during film compression. Also shown are the metal picrate extraction data for 18-crown-6 (○).

the film is in equilibrium with a subsurface bulk phase would be a function of the degree of complexation of the film. The data show that the collapse pressure goes through a clear minimum for a 0.1 M KCl subphase, and the plateau onset area increases when cations larger than lithium are present in the subphase. There is then a significant difference between the binding behavior of P18C6 in solution and at the air–water interface. While P18C6 in CH_2Cl_2 is able to extract Rb^+ and Cs^+ picrates from aqueous solution more efficiently than K^+ picrate, a film of P18C6 at the air–water interface appears to bind K^+ most strongly.

The data in Tables I and II are depicted in Figure 3 which graphically illustrates the relationship between the collapse pressure of the P18C6 monolayer and the selectivity of P18C6 toward Li^+, Na^+, K^+, Rb^+, and Cs^+ as determined by picrate extraction. This correlation suggests that, at the air–water interface, P18C6 does not bind larger alkali metal ions, Cs^+ and Rb^+, in a sandwich mode involving two crown moieties per metal ion. At the air–water interface, the conformation of the polymer is highly extended and crown moieties are likely to be oriented parallel to the water surface. Such a conformation will disfavor the sandwich orientations which facilitate formation of the 2:1 complex assumed to be necessary for efficient binding of Cs^+ and Rb^+ to the 18-crown-6 cavity of P18C6 in solution.

If the collapse pressure of films of P18C6 on solutions of alkali metal cations is indeed related to binding, then the collapse pressure should vary as a function of the concentration of ions in the subphase. One might even expect that two-dimensional binding constants could be obtained. In an effort to investigate these possibilities, compression isotherms for P18C6 on K^+Cl^- subphases of varying concentration were obtained (see Figure 4).

Compression isotherms of P18C6 spread on K^+Cl^- at 0.01–1.0 M show a single transition at the equilibrium collapse pressure of the films. This collapse pressure appears to decrease exponentially with the $[K^+]$ in the subphase and is linearized in a semilog plot (see Figure 5).

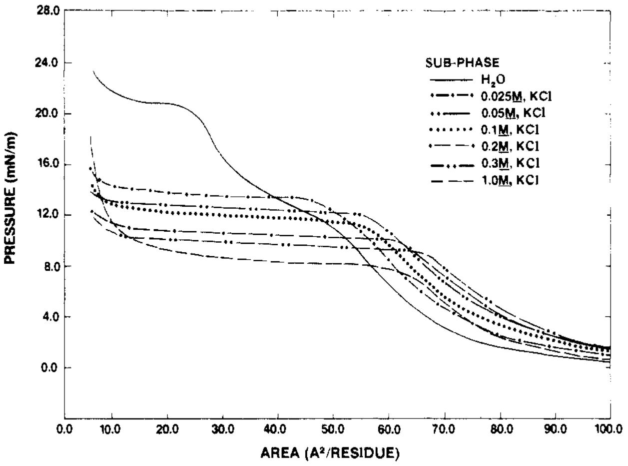

Figure 4. Compression isotherms (20 °C) for P18C6 spread on pure water ( ) and water of increasing K^+ ion concentration: [K^+ = 0.025 M (·–), 0.050 M (··–), 0.10 M (···), 0.20 M (·---·), 0.30 M (-···-), 1.0 M (––). Films were spread at 200 Å^2/residue and compressed at a rate of 13 Å^2/(residue·min).

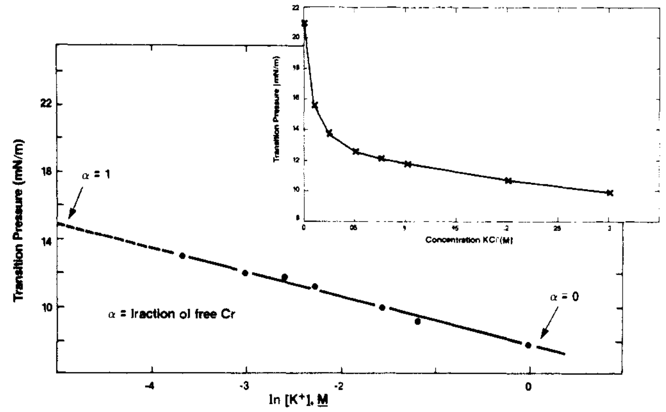

Figure 5. Variation of collapse pressure with $[K^+]$ in the subphase.

Table III. Binding Constants at the Air–Water Interface[a]

collapse pressure π, mN/m	$[K^+]$, M	α	K_1, M^{-1}
13.0	0.025	0.78	11.3
12.1	0.050	0.64	11.2
11.8	0.075	0.60	8.9
11.3	0.100	0.52	9.2
10.1	0.200	0.34	9.7
9.2	0.300	0.21	12.5
7.8	1.0	0	

[a] $K_1 = (1 - \alpha)/\alpha[K^+]$. α = 1 at 14.5 mN/m.

Assuming that the decrease in collapse pressure in directly related to the fraction of crown residues bound, 1 - α, where α = fraction of free crown residues, equilibrium constants can be evaluated at each subphase concentration. In making this calculation, we have arbitrarily taken the transition pressure at $[K^+] = 10^{-5}$ M as the collapse pressure at which α = 1. Similarly, α is assumed to be 0 at $[K^+]$ = 1.0 M in the subphase. The value of α at $[K^+]$ = 0.025, 0.050, 0.075, 0.10, 0.20, and 0.30 M is simply calculated from the ratio of the collapse pressure at any given $[K^+]$ to that at 10^{-5} M, 14.5 mN/m. Since the volume of the subphase solution is large, the concentration of K^+ in the subphase is not significantly depleted by binding to the monolayer. The two-dimensional binding constant is, thus, calculated on the basis of the equilibrium

$$K_1 = (1 - \alpha)/\alpha[K^+]$$

The values obtained average 10.5 M^{-1}, with a standard deviation of 12.4%. This value compares with a K_1 value of 18.5 M^{-1} for binding of K^+ to P18C6 in water.[19] Table III summarizes the data.

We have, thus, examined the π vs. A behavior of P18C6 on water, 0.1 M alkali metal salts, and 0.01–1 M K^+Cl^-. Our results show that the compression isotherms can be quantitatively related to the nature of the cation in the subphase and its concentration. At the air–water interface, the polymer is in a highly extended conformation, and cooperative binding between proximate crown ether groups is precluded. Accordingly, the binding characteristics of the polymer at the air–water interface mirrors that of the monomer benzo-18-crown-6 in solution and differs dramatically from that of P18C6 in solution.

Acknowledgment. We thank Ms. Anita VanLaeken of this laboratory for GPC characterization of poly(4′-vinylbenzo-18-crown-6) and Dr. David Tirrell (University of Massachusetts, dept. of Polymer Science and Engineering) for his careful and constructive review of the original manuscript.

Calculation of the Electronic Spectra and Excited-State Distortions of $W(CO)_5$(N-donor) from Preresonance Raman Intensities

Lee Tutt[†] and Jeffrey I. Zink*

Contribution from the Department of Chemistry, University of California at Los Angeles, Los Angeles, California 90024. *Received March 6, 1985*

Abstract: Excited-state distortions of $W(CO)_5$(pyridine) and $W(CO)_5$(piperidine) are calculated from emission spectra and preresonance Raman spectra by using the time-dependent theory of molecular spectroscopy. The time-dependent theory is described and the connections between electronic spectra and preresonance Raman spectra are discussed. The 10 K emission spectra and the preresonance Raman spectra of the two compounds are reported. Vibronic structure is observed in the spectra of both compounds. The crystal structure and the ground-state bond lengths are reported for $W(CO)_5$(pyridine). The excited-state distortions along 18 normal vibrational modes are calculated by using the combination of electronic spectroscopy, Raman spectroscopy, and time-dependent theory. The emission spectra are calculated from the preresonance Raman-determined intensities. The largest excited-state distortions are those which occur along the molecular axis containing the nitrogen donor ligand. These distortions are associated with the increase in antibonding along this axis caused by increased d_{z^2} σ antibonding in the excited state. In the case of $W(CO)_5$(pyridine), the W–N bond is lengthened by 0.18 Å, and the W-C bond trans to the pyridine is lengthened by 0.12 Å. The cis W–C bonds are only lengthened by 0.04 Å. The connections between the excited-state bond-length distortions and the photochemical reactivity of the molecules are discussed. The vibronic bands in the luminescence spectra of both molecules exhibit a new effect, the "missing mode effect" or MIME effect. Ground-state vibrational frequencies corresponding to the observed regularly spaced vibronic features in the emission spectra are missing. The origin of the MIME effect is explained.

The electronic emission and absorption spectra of large organometallic molecules in condensed media typically contain broad featureless bands. Spectra of these molecules at low temperatures sometimes reveal vibronic structure, but the individual vibronic components are usually not well-resolved. Instrumental resolution in these experiments is usually several orders of magnitude greater than the resolution seen in the spectrum. A typical example, that of the emission and absorption spectra of $W(CO)_5$(pyridine) at 10 K, is shown in Figure 1.

The information contained in the intensities and spacings of vibronic components of electronic spectra is important for understanding the properties of the excited and ground electronic states. Of particular interest in many spectroscopic and photochemical studies are the distortions the molecule undergoes upon electronic excitation.[1] However, detailed determination of excited-state structure via a Franck-Condon analysis, for example, is only possible when highly resolved spectra are available.[2-9]

Detailed calculations of excited-state distortions and structures and an intuitive understanding of the meaning of band widths and poorly resolved vibronic features are obtainable from the newly developed time-dependent theory of molecular spectroscopy.[10-12] In this theory, each vibrational degree of freedom and its displacement are explicitly considered. The theory connects preresonance Raman spectrsocopy, electronic absorption and emission spectroscopy, and geometry changes between the ground and excited electronic states. It has been applied to a limited number of transition metal and organic systems.[13-17]

The purpose of this paper is to combine preresonance Raman spectroscopy, which contains information complementary to electronic spectra, with the absorption and emission spectra to provide a detailed understanding of the excited-state distortions along the multidimensional excited-state potential surface. A new

---

[†] Current address: Hughes Research Laboratories, Malibu, CA 90265.

(1) Geoffroy, G. L.; Wrighton, M. S. *Organometallic Photochemistry*; Academic Press: New York, 1979.

(2) Hipps, K. W.; Merrell, G. A.; Crosby, G. A. *J. Phys. Chem.* **1976**, *80*, 2232.

(3) (a) Patterson, H. H.; DeBerry, W. J.; Byrne, J. E.; Hsu, M. T.; LoMenzo, J. A. *Inorg. Chem.* **1977**, *16*, 1698. (b) Patterson, H. H.; Godfrey, J. J.; Kahn, S. M. *Ibid.* **1972**, *11*, 2872.

(4) Urushiyama, A.; Kupka, H.; Degen, J.; Schmidtke, H. *Chem. Phys.* **1982**, *67*, 65.

(5) Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1978**, *17*, 1729.

(6) Rice, S. F.; Wilson, R. B.; Solomon, E. I. *Inorg. Chem.* **1980**, *19*, 3425.

(7) Wilson, R. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1980**, *102*, 4085.

(8) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951.

(9) Eyring, G.; Schmidtke, H. H. *Ber. Bunsenges. Phys. Chem.* **1981**, *85*, 597.

(10) Heller, E. J. *J. Chem. Phys.* **1975**, *62*, 1544.

(11) Heller, E. J. *Acc. Chem. Res.* **1981**, *14*, 368.

(12) Heller, E. J.; Sundberg, R. L.; Tannor, D. *J. Phys. Chem.* **1982**, *86*, 1822.

(13) Myers, A. B.; Mathies, R. A.; Tannor, D. J.; Heller, E. J. *J. Chem. Phys.* **1982**, *77*, 3857.

(14) Tutt, L.; Tannor, D.; Heller, E. J.; Zink, J. I. *Inorg. Chem.* **1982**, *21*, 3859.

(15) Yoo, C. S.; Zink, J. I. *Inorg. Chem.* **1983**, *22*, 2476.

(16) Tutt, L.; Tannor, D.; Schindler, J.; Heller, E. J.; Zink, J. I. *J. Phys. Chem.* **1983**, *87*, 3017.

(17) Yang, Y. Y.; Zink, J. I. *J. Am. Chem. Soc.* **1984**, *106*, 1500. Yang, Y. Y.; Zink, J. I. *Inorg. Chem.*, submitted for publication.

0002-7863/86/1508-5830$01.50/0