Photodissociation Spectroscopy of Methylnaphthalene Cations and the State Assignment of Naphthalene Ions

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Abstract: Photodissociation of 1- and 2-methylnaphthalene cations was studied from 12 500 to 45 500 cm^{-1} using ion cyclotron resonance detection and both arc lamp and laser sources. A number of peaks were observed in the photodissociation spectra, which were compared with theory, with solid-phase optical absorption spectra, and with photoelectron spectra, showing acceptable agreement in all cases. As compared with the solid phase, the gas-phase optical peaks are generally shifted by 1000 to 2000 cm^{-1} to higher energy. Spectra of the two isomers were in most respects similar: the peak shifts due to methyl substitution range from zero to about 2000 cm^{-1} and are accounted for in some but not all cases by simple perturbation arguments. Laser photodissociation spectra near 16 000 cm^{-1} did not show the pronounced vibrational splitting anticipated, and it appears that the prominent structure observed in matrix spectra is an effect peculiar to the solid-phase conditions. Correlation of information from all available techniques suggests that the state assignments for the naphthalene ion system are secure and well understood for the optically accessible states.

The capability of the new technique of photodissociation spectroscopy for obtaining optical spectroscopic information about gas-phase ions has added new possibilities to the spectroscopic study of radical ions.[2-6] Spectroscopic study of these species under gas-phase conditions offers the advantage of eliminating the sometimes difficult problems of distinguishing desired spectra from solvent and impurity absorptions; more significant, it opens the possibility of direct experimental separation of the effects of solvent or matrix on the spectra and energy levels of the ions. Most of the gas-phase work reported so far has been with small ions whose high reactivity makes them difficult to study in condensed phases. This report describes work on the naphthalene cation system, chosen because of its accessibility to study in both gas phase and condensed phase, as a convenient system for careful comparison. Actually picked for study were the two methylnaphthalene cation isomers, because the high endothermicity of photodissociation of the parent naphthalene cation makes it inconvenient for study. We will argue that the perturbation of the ion's spectroscopic behavior by the methyl group is relatively minor.

It has proven possible to obtain very satisfactory gas-phase photodissociation spectra of the methylnaphthalene cations over the visible and ultraviolet regions and to assign confidently the position and estimated intensities of the principal spectral transition of the gas-phase ions. The possession for the first time of this information without solvent (or matrix) perturbation and other uncertainties of condensed-phase spectra has encouraged us to reexamine the assignment of naphthalene radical-ion spectra. The result is a confirmation that the existing assignments are reasonable and consistent with all the available information and are strongly supported by the weight of experimental and theoretical evidence.

Experimental Section

Instrumentation and techniques followed closely what has been described in other recent photodissociation work.[7,8] Spectra were plotted from data obtained by the steady state kinetics approach, but a number of time-resolved photodissociation curves[7] were taken at various wavelengths, and were used to confirm the measurement of absolute cross sections and also to assure that the ion populations were spectroscopically homogeneous, that is to say that there was not a subset of ions showing radically different photodissociation properties. The indicated pressure of neutral was 3×10^{-8} Torr. The photoelectron spectrum of 1-methylnaphthalene was obtained with a Varian photoelectron spectrometer.

The laser photodissociation spectra were obtained using steady state ICR methods with illumination by a Coherent Radiation dye laser (Model 490) pumped by a model CR-12 Argon-ion laser.[6] Dyes used were Rhodamine-6G and Rhodamine B; sufficient power and stability of light output could not be achieved to extend the measurement further to the red than reported. Power output was in the range 0.5–5 W and was kept constant for the duration of acquisition of a given set of points, and the beam was expanded to several centimeters width. Problems were encountered with spatial and temporal variations in the beam in tuning over a wide range (problems which were accentuated by the Φ^2 dependence of photodissociation; see below), so that the spectra had to be pieced together out of numerous smaller segments overlapping at one or usually more wavelengths. The results reported average numerous scans of each wavelength region. Wavelengths were spaced 25 Å apart, which is much wider than the laser line width (<1 Å). We estimate the value of a data point relative to the average of neighboring points to be about ±10% (which gives ±5% for the uncertainty in a K_1 value as derived below and is the basis for our expectation that structure above the 5% level would probably have been clearly observed in these spectra).

Results and Discussion

The methylnaphthalene cations photodissociate according to

$$C_{11}H_{10}\cdot^{+} \xrightarrow{h\nu} C_{11}H_{9}^{+} + H\cdot \qquad (1)$$

Identical photodissociation spectra were obtained by observing the disappearance of parent ion or the appearance of $C_{11}H_9^+$, and most of the work to be discussed was carried out for parent ion disappearance.

Energetics. The energetics of the methylnaphthalene photodissociation reaction are known with reasonable confidence. Heats of formation of the 1- and 2-methylnaphthalene parent ions are precisely known from photoionization measurements,[9] while the heats of formation of the (P − 1) daughter ions are available from electron impact studies and are probably reliable to within 5 kcal. (The $C_{10}H_7CH_2$–H bond energy is taken as 76 kcal.[10]) These values yield endothermicities of 61 and 66 kcal for (1) for 1-methylnaphthalene and 2-methylnaphthalene cations, respectively, implying thermochemical thresholds of 2.13 μm^{-1} (4700 Å) and 2.33 μm^{-1} (4300 Å), respectively. Thus the photodissociation peaks observed near 2.7 μm^{-1} (3700 Å) and 3.7 μm^{-1} (2700 Å) are comfortably above the thermochemical threshold for both compounds.

However, the 1.6 μm^{-1} (6400 Å) region is clearly below threshold, and to account for the photodissociation observed here a sequential two-photon process of the kind postulated by Freiser and Beauchamp[11] seems necessary. The Freiser-Beauchamp mechanism involves sequential absorption of two photons into the appropriate electronic excited state, with rapid degradation of the first photon's energy into vibrational excitation of the still-bound parent ion. The spectrum obtained accurately reflects the photodissociation spectrum of the parent ion, but the apparent photodissociation rate is quadratic in light intensity (at high pressure and low light intensity[12]). That methylnaphthalene cation photodissociation in this wavelength region is in fact a two-photon process was clearly verified by the light intensity dependence of the observed photodissociation rate, which is clearly and accurately quadratic for both isomers over a substantial range of light intensities from about 10 to 100 mW/cm^2. The light-intensity dependence of the 2.7 μm^{-1} and 3.7 μm^{-1} regions was found to be linear, confirming that, as expected, photodissociation at these shorter wavelengths has a normal one-photon mechanism.

The methylnaphthalene cations thus present a situation which, it is now becoming apparent, is typical for photodissociation of many cations, in having two-photon photodissociation character at long wavelengths, crossing over to one-photon behavior at shorter wavelengths. This situation offers no serious obstacle to spectroscopic analysis of the data, as long as it is clearly recognized and appropriate equations are used for data reduction in the short- and long-wavelength regions.

Because of the uncertainty in the region of crossover from two-photon to one-photon behavior near ~2.2 μm^{-1} photodissociation between 2.2 and 1.9 μm^{-1} may not be accurately reflected; two-photon dissociation of the order of 2×10^{-18} cm^2 or less might well not be observed, while the detection limits for a one-photon process in this region are of the order of 1×10^{-19} cm^2.

Spectra. The photodissociation spectra are shown in Figure 1. In reducing these data, the region above 2.2 μm^{-1} was treated as appropriate for one-photon dissociation, with the observed dissociation rates being divided by the photon flux to yield photodissociation cross sections. The absolute cross section calibration above 2.2 μm^{-1} was determined by careful comparison of the methylnaphthalene cation photodissociation with toluene cation at 4000 Å (2.5 μm^{-1}), the cross section for toluene cation at that wavelength being taken as[13] 5.2×10^{-18} cm^2.

In the two-photon region below 1.9 μm^{-1} the data analysis is less straightforward, but the importance of making at least an estimate of the shape and intensity of this photodissociation peak justifies the following approximate treatment.

Taking the Freiser-Beauchamp mechanism,[11] we assume that the "effective" rate[14] of photon absorption by a ground state ion is $K_1\Phi$, where Φ is the photon flux and K_1 is a cross section, and that the vibrationally excited (activated) cation in the second photon absorption event absorbs at the same rate $K_1\Phi$ (so that $K_1 = K_2$ in Freiser and Beauchamp's terminology[15]). The rate K_3N of collisional deactivation of the activated cation is taken as equal to the ion-neutral collision rate,[16] using a collision rate constant of 2×10^{-9} cm^3/(molecule s). Freiser and Beauchamp show that at given pressure and light intensity, the two-photon photodissociation sequence gives an exponential ion density decay curve, with an observed rate

$$K_{\text{obsd}} = \frac{\Phi^2 K_1 K_2}{K_3 N + \Phi K_2} \simeq \frac{\Phi^2 K_1^2}{7 \times 10^7 P + \Phi K_1} \qquad (2)$$

where P is the pressure of neutral molecules in Torr, N is their number density, and the last expression on the right incorporates the assumptions made above about the present experiment. Accordingly the cross section K_1 may be readily obtained from a measurement of K_{obsd} by

$$K_1 = \frac{K_{\text{obsd}}}{2\Phi} \pm \frac{1}{2}\sqrt{K_{\text{obsd}}^2/\Phi^2 + 2.8 \times 10^8 P K_{\text{obsd}}/\Phi^2} \qquad (3)$$

$$\simeq \frac{8.4 \times 10^3}{\Phi}\sqrt{P K_{\text{obsd}}} \qquad (4)$$

where the last expression is appropriate to the high-pressure low-intensity conditions of this work. This exponential decay behavior means that there is no experimentally observed difference between one- and two-photon behavior at given pressure and light intensity, so that K_{obsd} may be obtained from the standard steady state photodissociation kinetic equations used extensively in previous work. Use of eq 4 then reduces K_{obsd} to the cross section K_1 for "effective" absorption of the first (or second) photon. It is K_1 which characterizes the desired optical-absorption spectral properties of the ion and is plotted in the appropriate portions of the spectra of Figure 1.

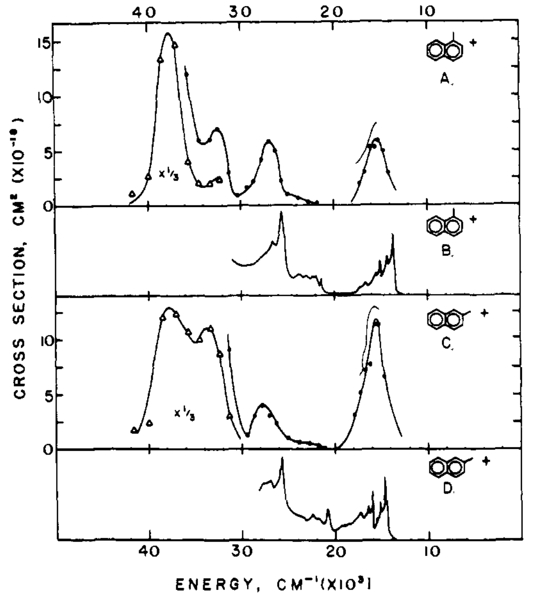


Figure 1. (A) and (C): photodissociation spectra of gas-phase methylnaphthalene cations. The short disconnected segments in the 16 000 cm^{-1} region indicate the laser data at a resolution of 25 Å (displaced upwards for display purposes). (B) and (D): optical spectra of the cations under glassy-matrix conditions.

Absolute calibration of K_1 values for two-photon dissociation using eq 4 is straightforward, the chief practical difficulty being the great sensitivity of the calculation to spatial inhomogeneity of the light beam. We considered this problem to be least severe for the laser experiment, in which the beam was expanded and homogeneous over most or all of the cell, and the absolute K_1 calibration in Figure 1 is directly taken from these data. The compounding of theoretical and experimental uncertainties leads to limited confidence in these numbers, which should be considered as order-of-magnitude estimates although the shape of the curve and the values of the points relative to each other should be quite accurate. (The one-photon cross sections, by contrast, should be accurate within 20 or 30%.)

These cross sections are for the process of "effective" photon absorption[14] of either the first or second photon, so that they are directly comparable to the one-photon photodissociation cross section at shorter wavelength. Thus for the entire spectrum, the cross sections given are equivalent to optical absorption cross sections *if* each absorbed photon eventually leads to dissociation and there are no other deexcitation mechanisms (fluorescence, phosphorescence, rearrangement, and so forth). As is always true in photodissociation spectroscopy the observed spectrum sets a lower limit to the optical absorption spectrum; the presence of a peak in the photodissociation spectrum guarantees the presence of an optical absorption of *at least* as great a cross section. Bearing this in mind, it is useful, as has been done in Figures 2 and 3, to indicate the molar absorptivity which corresponds to the observed cross section.

The partial spectra which could be obtained with the laser source at 25 Å resolution are shown in Figure 1 (displaced

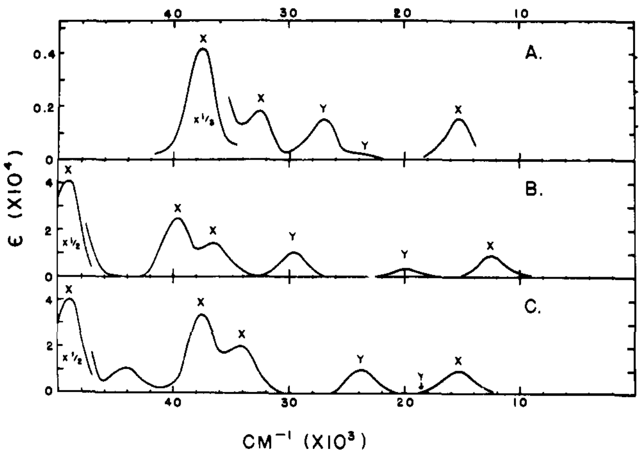


Figure 2. (A) Replica of curve (A) for Figure 1 showing the 1-methylnaphthalene photodissociation spectrum. (B) Theoretical spectrum of Shida and Iwata (ref 20). (C) Theoretical spectrum of Zahradnik and Carsky (ref 19).

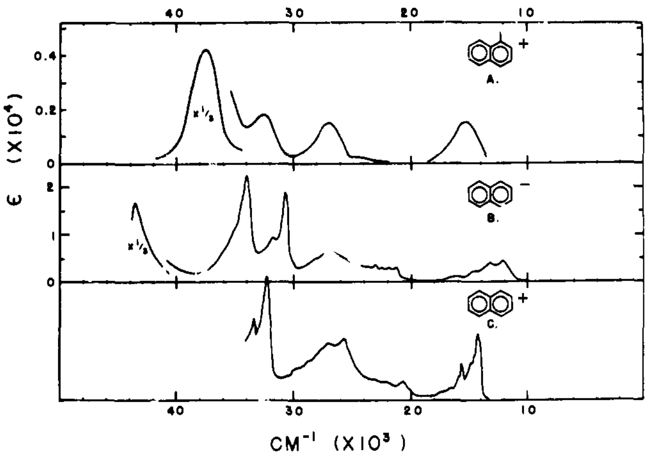


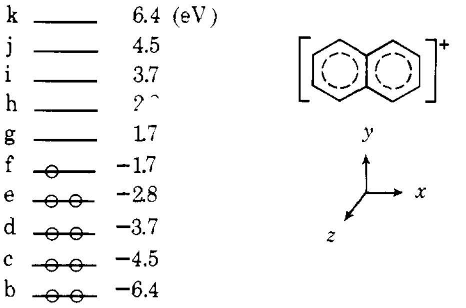
Figure 3. (A) Replica of Figure 1A. (B) Solid-phase optical spectrum of naphthalene anion (ref 20). (C) Solid-phase optical spectrum of naphthalene cation (ref 20).

slightly upwards for display purposes). Since data were taken at constant light intensity there is no uncertainty arising from an intensity correction; K_1 values for the two-photon process were obtained from eq 4. The shape of the curves agrees satisfactorily with the arc-lamp spectra. The main concern was whether vibrational structure could be resolved. As the figure suggests, the 1-methylnaphthalene cation curve was entirely smooth and featureless over the 1.55–1.75 μm^{-1} region; fine structure in the K_1 curve at a 5% level might have been observed, and at the 10% level would not have been missed. The 2-methylnaphthalene curve from 1.50 to 1.74 μm^{-1} does show some preliminary indication of barely resolved structure near the limits of experimental reliability. If real, this structure needs to be confirmed with experimental techniques substantially improved over present capabilities, and we consider the significance of the results at this stage to lie in the *absence* of pronounced vibrational features. As it is expected that these ions will be studied in detail with improvement in technique, no further comment need be made here.

The photodissociation spectra indicate the presence of four or five optical peaks for each of these cation isomers, with peaks in the vicinity of 1.5, 2.7, 3.3, and 3.8 μm^{-1}, and an apparent shoulder near 2.3 μm^{-1}. These are the first gas-phase spectral data to be obtained for these ions, and it is of interest to make a detailed comparison of these results with the rather different information available from photoelectron spectra and from solid-phase spectra, and with theoretical predictions. As will be seen, the photodissociation spectrum is largely consistent with all of these other sources of information and seems likely to be a good representation of the gas-phase optical spectrum of these cations from 1.25 to 4.55 μm^{-1}.

The spectra of the two isomers are in most respects similar. The intensity difference measured for the 1.5 μm^{-1} peaks between isomers is not outside a realistic assessment of the uncertainty in data reduction in the two-photon region and is probably not significant. The only difference significant within the precision of the data is the substantial difference in intensity in the peak near 3.3 μm^{-1}. The origin of this difference is not clear and may arise either from differences in absorption cross section or from a differing probability of photodissociation vs. fluorescence or other processes, but it is useful in that it clearly shows the 3.3 and 3.8 μm^{-1} peaks to be distinct. Unfortunately, lack of light intensity made it impossible to obtain reasonable data above 4.2 μm^{-1}, although we can say with some confidence that the intensity at 4.35 and 4.55 μm^{-1} is not *greater* than that at 3.85 μm^{-1} and seems likely to be substantially smaller, as expected from theory.

Scheme I



Comparison with Theory. The 10 Π molecular orbitals of naphthalene are denoted in Scheme I, with electron occupation as in the ground state cation, and with orbital energies estimated from the HMO energies using[17] $\beta = 2.8$ eV. Of the numerous possible one-electron excitations only a few are of possible optical importance, the others being either parity forbidden or excessively high in energy:[18] The excitations c → f (I_3, 2.32 μm^{-1}) and f → g (A, 2.82 μm^{-1}) give low-lying transitions of *y* polarization, while somewhat higher are a pair of transitions, also of *y* polarization, contributed by the e → h (B, 4.65 μm^{-1}) excitation. In x polarization are the low d → f (I_2, 1.66 μm^{-1} excitation and three close transitions contributed by the (degenerate) f → h (B, 3.74 μm^{-1}) and e → g (B, 3.74 μm^{-1}) excitations (the latter of which gives two doublet → doublet transitions). The transitions of like symmetry interact, in particular the three last-mentioned B transitions near 3.74 μm^{-1} which are of the same symmetry and nearly the same energy, so that a good configuration-interaction treatment is essential for any kind of quantitative prediction of energies and intensities. Zahradnik and Carsky[19] have made a series of careful calculations on this system with various configuration interaction approaches, without much variation in the results. Shida and Iwata[20] have also reported a calculation at a similar level, which yields results which are qualitatively similar but somewhat different in calculated peak positions for transitions of both allowed symmetries. Results of both of these calculations are compared with the 1-methylnaphthalene cation photodissociation spectrum in Figure 2. In order to make comparison convenient, an arbitrary line width of 0.28 μm^{-1} was assumed with Gaussian line shape for all the theoretical peaks, and the resulting theoretical spectrum was traced with a DuPont curve resolver. This permits a comparison of absolute molar absorptivity values between theory and experiment.

On the basis of Figure 2 alone, assignment of the photodissociation spectrum would be at best uncertain, because of the

Table I. Optical Peaks in Naphthalene Ions (10^3 cm^{-1})

Optical transition[a]	1-Methylnaphthalene		2-Methylnaphthalene		Naphthalene	
	Gas[b]	Solid[c]	Gas[b]	Solid[c]	Anion[c,d] (solid)	Cation[c] (solid)
I_2	15.4	14	15.6	15.5	13	15
I_3	~25	~23	~24	~22	~23	~22
A	26.9	26	27.7	26	27	26
B_1	32.6		33.7		30.5	32.5
B_2	37.7		37.9		34	

[a] See ref 18. [b] This work. [c] Reference 20. [d] Reference 21.

multiplicity of peaks and the uncertainty in the theoretical predictions. As will be made clear, the additional information from photoelectron spectra and condensed-phase spectra is important in making an unambiguous match of theoretical and experimental peaks.

Condensed-Phase Spectra. Spectra of a number of relevant ions in glassy media at low temperature have been obtained by Hoijtink et al.[21,22] and most recently by Shida and Iwata.[20] There are some points of interest in comparing the spectra of the methylnaphthalene anions[20] with the present results, but we have chosen for careful comparison the spectra of the methylnaphthalene cations themselves, and also the naphthalene cation and anion (only for this last ion do reliable and intensity-calibrated spectral data exist over the full wavelength range accessible to the photodissociation experiment). These spectra are reproduced in Figures 1 and 3.

Table I summarizes the optical peaks and features observed in all the spectra, with the tentative assignments suggested in the preceding section. In this table, an attempt has been made to locate the approximate smoothed center of the optical features, which of course is rather uncertain for peaks like the structured 1.5 μm^{-1} solid phase peaks and for the very poorly defined feature around 2.4 μm^{-1}. Still, this comparison seems valuable within its limitations. All of the solid spectra are similar in their features, with a structured, asymmetric peak near 1.4 μm^{-1}, a broad low shoulder from 2.0 to 2.4 μm^{-1}, a (split) peak near 2.6 μm^{-1}, and two strong peaks between 3.0 and 4.0 μm^{-1}. The measurements of Hoijtink et al.[21,22] on the polarization of photobleaching support the assignment given.

The principal features of the photodissociation spectra are readily matched with this pattern, feature for feature. The gas-phase photodissociation spectra show an average blue shift of the order of 0.1 μm^{-1} relative to the corresponding solid-phase spectra. There is no evident pattern to the blue shifts for the various peaks, which clearly reflect some degree of matrix red shifting. The relative intensities of the different peaks are qualitatively consistent from solid to gas phase.

The shifts arising from methyl substitution are relatively small. A small shift in the 1.4 μm^{-1} peak between isomers is indicated by the solid-phase spectra and qualitatively reflected in the photoelectron and photodissociation peaks. Both gas and solid spectra suggest a 0.1 μm^{-1} shift between isomers in the 2.4 μm^{-1} peak, while the gas-phase results suggest shifts of the order of 0.1 μm^{-1} in the 2.7 and 3.3 μm^{-1} peaks, the former not supported by the solid-phase results. A simple perturbation treatment[19,23] along lines similar to those used for methyl-substituted benzene cations suggests that the energy difference in transitions of 1- and 2-methylnaphthalene cations should be negligible for the I_2 and A transitions, while the B transitions should be shifted by about 0.1-0.2 μm^{-1} to the red and the I_3 transition by a similar amount to the blue in 1-methylnaphthalene cation as compared with the 2-methyl derivative. The perturbation treatment therefore accounts qualitatively for the observed differences in I_3, B_1, and B_2 and for the similarity in the A transition between the isomers, while predicting a smaller shift than observed for I_2.

A surprising feature is the failure to observe prominent structure in the gas-phase 1.5 μm^{-1} peak with the laser source. The laser wavelength resolution is, presumably, much better than necessary, and there is no evident reason for the two-photon mechanism to lead to serious suppression of vibrational structure. The present limited amplitude precision of the laser experiments does not rule out structure lost in the noise at a 5 or even 10% level but definitely excludes the kind of prominent structure which was expected from looking at the condensed-phase spectra. The photoelectron spectra of the neutrals, discussed below, similarly show no evidence for prominent resolved vibrational structure in this band, and it seems highly likely that much of the extensive structure shown in the matrix spectra is peculiar to this medium. It is possible that the low-temperature glass environment enhances the vibrational structure of the band relative to gas phase, or alternatively that the observed structure is not vibrational structure but rather reflects matrix splitting of the peak. More work, including extension of the laser results farther to the red to encompass the 0-0 transition, is certainly required to make sense of this observation.

The very satisfactory agreement among all the spectra obtained for cationic species is encouraging, lending strong support to the hypothesis that neither the methyl substituent nor the fact that the present spectra are not direct absorption spectra is of critical importance and that we have now an excellent view of the spectrum of the gas-phase naphthalene radical cation system. The position and qualitative intensity of the 3.8 μm^{-1} peak, previously inaccessible in cation spectra, is then almost certainly reliable as a feature of the naphthalene cation spectrum.

The comparison with the naphthalene anion spectrum[20] is also interesting, because the condensed phase spectrum extends all the way to 4.5 μm^{-1}. As is seen in Figure 3, the spectrum is qualitatively similar to the photodissociation spectra in the position of the peaks, as expected, and also in their intensity. The three x-polarized peaks are strongly red shifted (by over 0.3 μm^{-1}) in the condensed phase anion spectrum, but as far as can be told from the rather ill-defined anion peaks, the y-polarized peaks near 2.4 and 2.7 μm^{-1} are shifted hardly at all, as noted by Shida and Iwata.[20] Unfortunately, in the absence of a gas-phase anion spectrum, there is no way to tell to what extent these shifts are matrix induced and how much they represent quantitative failure of the pairing theorem. It is clear that qualitatively the pairing theorem holds up very well.

Photoelectron Spectra. The basis for comparing photoelectron spectra with gas-phase cation spectra is well known. It is important to note that photoelectron spectra are normally expected to show strong peaks corresponding to removal of a single electron from the neutral, without simultaneous excitation of another electron. In the spectral terminology used here, this means that photoelectron spectra show strong peaks corresponding to I-type excitations but not corresponding to

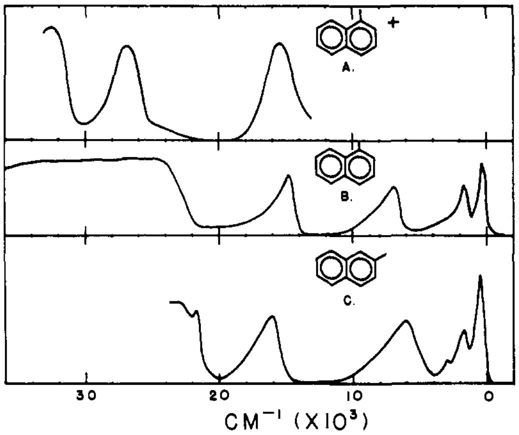


Figure 4. (A) Replica of Figure 1A. (B) Photoelectron spectrum of 1-methylnaphthalene. (C) Photoelectron spectrum of 2-methylnaphthalene (ref 24).

A- and B-type excitations. This point has been discussed in connection with spectra of benzene cation derivatives[5] and is a useful aid in making assignments.

In the naphthalene cation, there are two allowed I-type transitions in the visible-uv region, the I_2 (d → f) transition near 1.5 μm^{-1} and the I_3 (c → f) transition near 2.3 μm^{-1}. The photoelectron spectra of both methylnaphthalenes[24] are shown in Figure 4, with the first IP set at the energy zero, as is appropriate for spectral comparisons. The peak 1.5 or 1.6 μm^{-1} clearly corresponds to the optical I_2 excitation.

The photoelectron spectra of both methylnaphthalenes (Figure 4) and naphthalene itself suggest that there is no PES-observable state between 1.5 μm^{-1} and 2.3–2.4 μm^{-1}. Eland and Danby[17] make the assignment, which we consider very reasonable, that the PES peak at 2.4 μm^{-1} corresponds to I_3, in almost exact agreement with simple Hückel excitation energies. This corresponds well to the low-intensity feature in the optical spectra at ~2.4 μm^{-1} (gas-phase photodissociation), ~2.3 μm^{-1} (condensed-phase cations), and ~2.1–2.5 μm^{-1} (anion). This is consistent with an assignment of the stronger y-polarized peak at 2.7–2.8 μm^{-1} (gas phase) as the A transition, which, even if it were expected to appear in the PES spectrum, which it is not, would be masked by σ-orbital peaks.

The other Π transitions I_1 and I_4 are not in the optically accessible region and are optically forbidden, so that no further correspondence is expected between optical and PES features in these cations.

Conclusions

A combination of all the considerations discussed above indicates that the electronic-level assignment of the naphthalene cation system is as given in Table I, with high confidence. The only element in this picture which is not fully satisfactory is the less-than-perfect agreement of experiment and theory; since the two calculations shown in Figure 2 disagree with each other as much as with experiment, it is clear that the available theoretical approaches need refinement. The interacting pair of y-polarized bands seem to give particular difficulty: Zahradnik and Carsky have used an interaction giving realistic splitting, but place the peaks too low, whereas Shida and Iwata obtain a better average position but an unrealistically large splitting. Since the experimental situation seems well established, a reexamination of the energy and interaction terms would seem appropriate.

The naphthalene case is an excellent illustration of the variety of complementary techniques now available for study of the excited states of radical cations. (1) Current theoretical methods can give the number of states of each symmetry, with approximate estimates of the energies and optical intensities of each. The naphthalene case would suggest that a good calculation might give energies to ±0.4 μm^{-1} and intensities within a factor of 2 or 3. (2) Condensed-phase spectra can give a direct optical absorption spectrum of the cation (and, for alternant systems, the equivalent anion) with direct determination of the optical polarization of each peak and, sometimes, the absolute absorptivities. Drawbacks are the unknown perturbing effect of the matrix or solvent and the frequent interference of solvent and impurity absorptions. (3) The photoelectron spectrum of the neutral selectivity displays the I-type excitations, giving accurate gas-phase energies for these states (when vibrational effects are correctly accounted for) and often vibrational structure. (4) The photodissociation spectrum of the cation gives accurate gas-phase energies of optically allowed states from ~1.0 to ~4.5 μm^{-1}. The absolute cross sections obtained can give an indication of the optical absorptivity, although they are in principle only lower limits. The potential of this approach for observing vibrational structure is only beginning to be exploited.[6]

The naphthalene case exemplifies the situation which will hold for many cationic species, in that taken separately any of these approaches can provide only fragmentary and ambiguous characterization of the cationic electronic states, but taken together they allow a convincing characterization and assignment of the electronic states and transitions of the cation. These ideas should see fruitful application to a variety of cationic species.

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(15) This is not necessarily a good assumption. Not only does it depend on equal first-photon and second-photon absorption cross sections, but, also, as pointed out by Freiser and Beauchamp, it may be poor in an inhomogeneous light beam. In these experiments the laser beam was spread out to ensure reasonable homogeneity, so that the inhomogeneity effect is not expected to be severe. Since the ion absorbing the second photon is in the same (ground) electronic state as the initial ion and differs only in its vibrational excitation, there is no reason to expect major differences in its absorption intensity, although differences can certainly not be ruled out. Beyond this, the assumption can mainly be justified as an expedient likely to serve well

enough for most purposes. A fuller analysis of the general two-photon kinetics scheme is being prepared for publication and indicates that separate K_1 and K_2 determination is at best very difficult and that the determination of K_1 is in any case not critically sensitive to the K_1/K_2 ratio.
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Resonance Raman Studies of Macrocyclic Complexes. 1. Structural and Electronic Effects in Synthetic Metal(II) Porphyrin Analogues

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Abstract: Resonance Raman spectra are reported for the Mn(II) ($s = 5/2$), Fe(II) ($s = 1$), Co(II) ($s = 1/2$), Ni(II) ($s = 0$), Cu(II), and Zn(II) complexes of the dianionic, π-delocalized N_4 macrocyclic ligand 5,7,12,14-tetramethyldibenzo[*b,i*]-[1,4,8,11]tetraazacyclotetradecahexenate (L^{2-}). The resonance Raman spectrum of H_2L is also discussed. All of the A_1 normal modes of the carbon–nitrogen–metal skeleton of $M^{II}L$ are observed among the resonance Raman spectra of the six complexes studied. Vibrational assignments are made for these modes. The assigned vibrations are correlated among the $M^{II}L$ complexes, revealing substantial metal-dependent shifts in ligand vibrational frequencies. The vibrations which exhibit large shifts are associated with the porphyrin-like six-membered chelate rings. These frequency shifts are, in some cases, attributable to electronic (as opposed to structural) effects of the d orbital occupancy of the metal ions. Structural effects upon Raman *intensity* as well as the frequency of ligand modes are observed for $Mn^{II}L$. This complex is distorted due to considerable displacement of the metal ion out of the N_4 coordination plane. Although the peripheral methyl substituents of $M^{II}L$ are not part of the chromophoric π system of the ligand, the Raman scattering due to the methyl group vibrations is nevertheless strongly resonance enhanced. It is suggested that this is a hyperconjugative effect. Selective Raman intensity enhancement of either ligand-centered or metal-associated vibrations is observed when laser excitation is chosen within respectively $\pi \rightarrow \pi^*$ or charge-transfer electronic transitions of $M^{II}L$. The results suggest (a) that metalloporphyrin frequency shifts may be due to electronic as well as structural effects of the metal ion, (b) that vibrations of peripheral alkyl substituents must be considered in assigning resonance Raman spectra of π-delocalized macrocycles, and (c) that selective Raman intensity enhancement may have utility in assigning metal–ligand modes in natural and synthetic macrocyclic complexes. Raman intensity patterns which have important implications in the theory of the resonance Raman effect are observed, and these are discussed in the following paper.

Much of the wide interest in synthetic macrocyclic complexes is a consequence of their relationship to naturally occurring macrocycles, particularly metalloporphyrins.[1] The cyclic Schiff base formed from acetylacetone and *o*-phenylenediamine (H_2L, Figure 1a) shares many common characteristics with porphyrins.[2-6] It forms tetradentate, N_4-coordinated metal complexes in which the ligand deprotonates to form L^{2-}. In these complexes L^{2-} possesses an extensively delocalized (24 electron) π system, and the electronic spectra are dominated by in-plane, $\pi \rightarrow \pi^*$ electronic transitions. The six-membered chelate rings in the L^{2-} complexes are structurally similar to those of metalloporphyrins and undergo analogous structural distortions to accommodate metal ions of various sizes.[3,4,6-8] Complexes of L^{2-} with a wide variety of metal ions have been synthesized.[3,5,9,10] These complexes offer an opportunity to study systematically the effects of metal electronic configuration, size, charge, and chemical parameters upon the structure and properties of the delocalized, macrocyclic ligand framework.

The resonance Raman effect may be observed when the Raman excitation frequency corresponds to an electronic transition of the scattering system.[11] Under this condition, the Raman scattering intensity of vibrations which couple with the electronic transition can be resonance enhanced by several orders of magnitude.[12] Resonance Raman spectroscopy has proven to be a powerful probe for structure and bonding in chromophoric groups,[13] particularly in corrins, hemes (including heme proteins), and metalloporphyrins (including those with various biomimetic characteristics).[14-17] However, the resonance Raman effect has not previously been applied to synthetic macrocyclic complexes. We now report resonance Raman studies of H_2L and a series of $M^{II}L$ complexes, where M is manganese, iron, cobalt, nickel, copper, and zinc.

Several characteristics of L compared to porphyrins have proven to be illuminating in these studies. First, the relatively simple structure of L allows vibrational assignments to be made with confidence. Second, the lowest energy $\pi \rightarrow \pi^*$ electronic transitions of L are in the near ultraviolet rather than in the visible as is the case with porphyrins.[18] Therefore, for $M^{II}L$ complexes having metal-centered electronic transitions in the visible region, resonance Raman effects due to these transitions are separable from those due to the ligand $\pi \rightarrow \pi^*$ spectrum. Thus, the structural and electronic effects of the metal upon the resonance Raman spectra are more easily interpretable for the $M^{II}L$ complexes than for metalloporphyrins or other naturally occurring macrocycles. This report is concerned primarily with these structural and electronic effects. The unusual resonance Raman intensity patterns observed for certain $M^{II}L$ complexes, and the interpretation of these intensity patterns, are the subject of the following report.[19] Our results have important general implications concerning vibrational studies of natural and synthetic metallomacrocycles and also illuminate