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Nitric oxide photofragment rotational distribution from UV dissociation of cyclopentadienylnickel nitrosyl

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The rotational state distribution for NO produced by dissociation of $(\eta^5\text{–}C_5H_5)NiNO$ near 225 nm has been obtained by [1 + 1] resonance-enhanced multiphoton ionization. The distribution is approximately characterized by a Boltzmann distribution at $T = 900 \pm 200$ K. The relative populations of the two spin–orbit components of the ground $^2\Pi$ manifold are also consistent with this temperature. No preference is observed for populating either of the lambda–doublet components, even at high rotational quantum numbers. Comparison of the results with statistical models shows that the state distribution is significantly colder than expected. One plausible explanation for this is that the parent molecule dissociates to produce cyclopentadienylnickel fragments in an excited electronic state.

INTRODUCTION

The spectroscopy and photochemistry of transition metal complexes are of current interest from the standpoint of learning about chemical bonding and molecular dissociation in this important class of molecules. One of the general characteristics of transition metal complexes is the diffuseness of their ultraviolet absorption bands.[1] This diffuseness may remain even upon cooling in supersonic beams[2] or cryogenic matrices.[3,4] Consequently, conventional spectroscopic methods are of limited usefulness for characterizing the nature of excited electronic states.

Photofragment spectroscopy provides a powerful alternative approach to learning about metal–ligand bond scission in these systems. Wietz and co-workers[5,6] have successfully elucidated fragmentation patterns and recombination rate coefficients for $Fe(CO)_5$ and $Cr(CO)_6$. Waller *et al.*[7] used laser-induced fluorescence to determine rotational and vibrational distributions of CO produced by dissociation of $Fe(CO)_5$. The distributions were consistent with a statistical calculation, implying the lack of dynamical constraints in the disposal of available energy among the photofragments. Rosenfeld and co-workers[8] have employed an infrared transient absorption technique for determining rotational and vibrational distributions of CO fragments from UV dissociation of metal carbonyls. These workers have also found that in many cases, fragment state distributions are statistical.

In this study we report the nitric oxide rotational state distributions resulting from ultraviolet dissociation of cyclopentadienylnickel nitrosyl (hereafter, CpNiNO). This compound has only two ligands of widely different characteristics so that contributions from different photodissociation mechanisms is minimized. A preponderance of evidence indicates that the experiment only probes dissociation of NO directly from the parent compound following single photon excitation. The rotational and spin–orbit distributions of the NO photofragments are found to be approximately characterized by a Boltzmann distribution at 900 ± 200 K. This distribution is significantly colder than expected from a statistical partitioning of available energy, and is consistent with formation of the CpNi fragment in an electronically excited state.

EXPERIMENTAL

Dissociation of the parent compound and ionization of the NO photofragments is accomplished in a single pulse (i.e., one-color experiment) from an excimer-pumped dye laser (Questek model 2200 excimer at 308 nm; Lumonics EPD-330K dye laser). Ultraviolet radiation near 225 nm is generated by frequency doubling the dye laser output in a potassium pentaborate (KB5) nonlinear optical crystal (Interactive Radiation, Inc.). The crystal is maintained at the optimum phase matching angle via a home-built feedback circuit. The pulse energy used in the experiments is approximately 50 μJ and is monitored by detecting fluorescence of a sodium salicylate coated window with a photodiode detector.

The laser beam is focused with a long focal length lens (0.5 or 1.0 m) into the source region of a quadrupole mass spectrometer. The CpNiNO is admitted via an effusive inlet and maintained at a constant pressure of about 3×10^{-4} Pa. Fragment ions produced by the laser are mass selected and detected by a secondary electron multiplier. The signal is amplified and processed by a boxcar signal averager, and is finally sent to a chart recorder. The resonance-enhanced multiphoton ionization (REMPI) spectrum of NO is obtained by monitoring the ion signal as a function of laser wavelength in the region 224–227 nm. During each scan, the laser pulse energy is kept constant to within 10% of its mean value.

CpNiNO was obtained from Strem Chemical and purified by repeated freeze–pump–thaw cycles before each experiment. Its UV absorption spectrum was obtained using a 10 cm gas cell in a Varian model Cary 17 absorption spectrometer. Decomposition of the parent compound was found to be minimal, even after prolonged storage. Nitric oxide (Matheson) was purified by passing through silica gel[9] at 170 K followed by pumping on the solid at 77 K.

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RESULTS

The ultraviolet absorption spectrum of CpNiNO exhibits two broad, unstructured bands peaked near 283 and 199 nm. Excitation of the complex at 224–227 nm induces dissociation, presumably to CpNi + NO. This point will be addressed in more detail in the following section. The 224–227 nm region is also the proper range over which individual rotational states of NO($v = 0$) may be probed by [1 + 1] REMPI via the $A\ ^2\Sigma^+$ excited state. Accordingly, when the dye laser is scanned over this region while the compound is present in the mass spectrometer chamber, a strong wavelength-dependent ion signal is recorded at $m/e = 30$ amu (NO^+). A representative spectrum is presented in Fig. 1. Because we utilize only one laser in the experiment, it is not possible to avoid changing the excitation wavelength while scanning the NO photofragment spectrum. However, the photon energy changes by only about 1% over this range, and absorption coefficient for CpNiNO changes by less than 3%. In view of the fact that the absorption bands are broad and unstructured, the small change in excitation wavelength over the course of the experiment is believed to be inconsequential. The spectra themselves give no indication that this small change in excitation wavelength has any effect on the dissociation mechanism.

The functional dependence of the ion signal on average pulse energy was found to be linear (within 20%) when NO photofragments from CpNiNO were probed at the $R_{22}(J = 5.5)$ line in the REMPI spectrum. A check of the same line in the spectrum of pure NO at 300 K showed that the REMPI signal is also linear with power under our experimental conditions. However, other lines in the spectrum of thermal NO were found to have various power dependences ranging from linear to quadratic. Due to a limited quantity of CpNiNO (the compound is no longer available commercially) we did not make a systematic study of the power dependence of each spectral line.

Instead, several REMPI spectra were obtained for NO from CpNiNO using two different lenses (0.5 and 1.0 m focal lengths) at the same nominal pulse energy. The laser power in these two experimental setups differs by approximately a factor of 4. There are, indeed, significant differences in the relative peak heights in the spectra obtained with the two lenses. However, all of these differences are attributable to laser power dependent saturation and alignment effects in the REMPI spectrum of NO. When the spectra are corrected for these effects (*vide infra*), the rotational state distributions obtained for spectra obtained with the two different focal length lenses are the same, within experimental uncertainty. This is an important result because, as shown in the following section, it indicates that dissociation of the CpNiNO occurs upon single photon excitation (or, at least, the rotational distributions are insensitive to multiphoton effects).

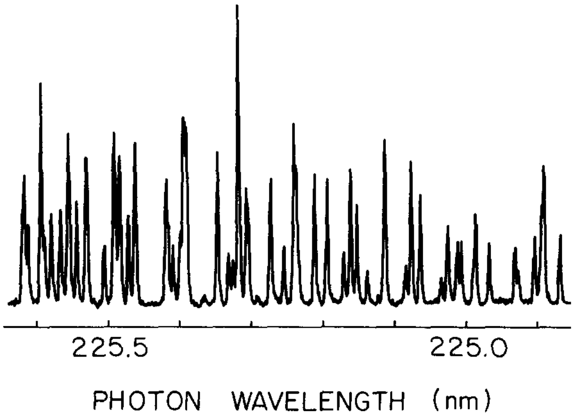

FIG. 1. A portion of the [1 + 1] REMPI spectrum of NO photofragments from CpNiNO obtained with a 0.5 m focal length lens.

The spectrum shown in Fig. 1 probes rotational states of NO photofragments in the $v = 0$ level. Fragments in $v = 1$ may be probed at longer wavelengths (in the 0–1 band near 236 nm) or at shorter wavelengths (in the 1–1 band at 222–224 nm). We have observed transitions due to $v = 1$ rotational states near 224 nm, but the procedure for extracting state distributions from the REMPI spectra is much less reliable for $v = 1$ compared with $v = 0$. Also, the experimental setup for second harmonic generation was not capable of obtaining the entire $v = 1$ spectrum. Therefore, the analysis presented in this paper is directed exclusively at the rotational distribution in $v = 0$.

As mentioned above, the principal difficulties in extracting rotational state populations from REMPI spectra arise from the interdependent effects of saturation and intermediate state alignment. As a result, different branches of the spectrum yield somewhat different apparent populations and state distributions (temperatures). These effects have been discussed in detail by Zare *et al.*,[10] who have also provided a detailed procedure for correcting the spectra.[11] Unfortunately, this procedure requires obtaining massive amounts of experimental data in order to characterize the saturation and alignment characteristics for each experimental setup.

We have chosen a more pragmatic approach to the problem by obtaining REMPI spectra of NO from CpNiNO and of pure NO under identical experimental conditions. For transitions arising from relatively low-lying rotational states ($E_{\rm rot} < 1000\ {\rm cm}^{-1}$) the intensities of lines in the CpNiNO spectrum (as measured by peak heights) are compared directly with corresponding lines in the spectrum of pure NO at 300 K. The populations of the rotational states at thermal equilibrium can, of course, be calculated exactly. Therefore the populations of low-lying rotational states of the NO photofragments from CpNiNO were determined using Eq. (1)[12]

$$N'(J) = (I'/I)(2J+1)\exp[-E_{\rm rot}(J)/kT], \qquad (1)$$

where I and I' are the measured intensities of a line arising from rotational state J in the thermal and photofragment NO spectra, respectively, and $T = 300$ K. For high J states ($E_{\rm rot} > 1000\ {\rm cm}^{-1}$) the bands in the thermal NO spectrum were too weak to measure accurately. The value of I in Eq. (1) for these states was estimated by linear extrapolation of the Boltzmann plot for each branch of the 300 K spectrum. These plots were constructed using the Hönl–London factors given by Bennett.[13] The NO photofragment rotational state distributions from CpNiNO determined using this procedure are presented in Fig. 2. Uncertainties in the populations are indicated by the error bars (representing ± 1 standard deviation) at representative points in the figure.

It is worthwhile to point out several aspects of the state distributions presented in Fig. 2. First, the populations are consistent with a rotational temperature in the photofragments of 900 ± 200 K, indicated by the straight line. The quoted uncertainty represents one standard deviation. Secondly, the relative population of the two spin–orbit components of the ground state is found to correspond to a temperature of 800 ± 320 K. The fact that the rotational and spin–orbit temperatures are the same within experimental uncertainty is underscored by the fact that populations arising from both spin–orbit states lie along the same line in Fig. 2. Note that E_{rot} (abscissa in Fig. 2) is defined as the sum of the rotational and spin–orbit energies relative to the $J = 0.5$ level of the $^2\Pi_{1/2}$ manifold.

Although not shown explicitly in Fig. 2, the apparent rotational state populations determined from various branches of the REMPI spectrum are the same, within experimental uncertainty. We can draw two important conclusions from this observation. First, since the transition moments for the various branches of the spectrum have different orientations with respect to the total angular momentum vector J, the NO photofragments are not preferentially aligned with respect to the laser polarization axis. This means that the photofragments are scattered isotropically. Secondly, since each branch of the spectrum probes one of the two lambda–doublet states of NO, we conclude that no preference is observed for selective population of either of these states. Previous studies[14,15] have shown that selective population of lambda-doublet states is possible when the photofragments are produced in high J states corresponding to Hund's case (b).[16]

DISCUSSION

Before addressing the interpretation of the rotational state distributions, it is important to consider two important issues regarding the mechanism for photodissociation of CpNiNO. The first is whether or not the parent molecule is excited by a single photon or multiple photons. The second is whether the fragment NO arises from dissociation of CpNiNO as a primary process, or from secondary fragmentation of NiNO following initial loss of the cyclopentadienyl ligand.

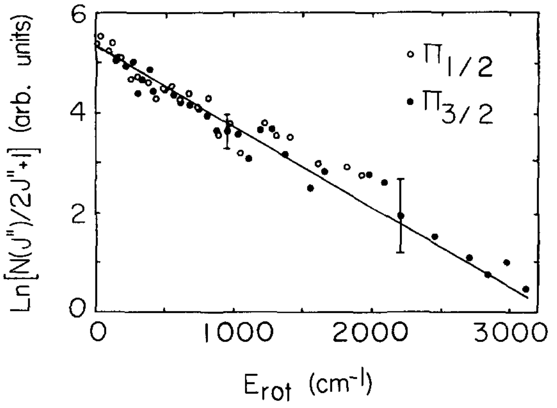

FIG. 2. Rotational state distribution of NO photofragments from CpNiNO presented in the form of a Boltzmann plot. The open circles denote states of the lower $^2\Pi_{1/2}$ spin–orbit manifold whereas the solid points correspond to $^2\Pi_{3/2}$ states. The error bars ($\pm 1\sigma$) are larger for points at $E_{\text{rot}} > 1000$ cm^{-1} due to the extrapolation procedure described in the text. The straight line represents a temperature of 900 K.

Taking first the issue of single vs multiphoton excitation, the most common technique for assessing the role of multiphoton excitation is to determine the functional dependence of the signal on laser power or laser fluence. A spot check of the R_{22} ($J = 5.5$) line showed that both the thermal NO and NO photofragment signals are approximately linearly dependent on laser power. However, at least three photons are required to form NO$^+$ in the photofragment spectrum (one to excite the parent molecule and two more to ionize the NO fragment). Therefore, measurements of the power dependence of the ion signal are of limited usefulness for establishing whether the parent molecules are excited by one or more photons prior to dissociation of NO.

A more significant indication of the single photon nature of the parent molecule excitation is that the photofragment NO rotational state distribution is found to be the same when the laser was focused with either a 0.5 or 1.0 m focal length lens. There are, of course, differences in the raw spectra obtained in these two different experimental setups, but each photofragment spectrum is analyzed using a spectrum of pure NO obtained under identical conditions. The resulting state distributions are independent of the fourfold change in laser fluence caused by using the different lenses. Since each photon deposits about 44 000 cm^{-1} of energy into the molecule, we expect that the state distributions should be strongly influenced by the presence of multiphoton excitation. The absence of such effects is good evidence that the parent molecule absorbs only a single photon prior to breaking the Ni–NO bond.

Next, we consider some of the consequences of dissociation mechanisms involving loss of more than one ligand from the parent molecule. The problem is particularly acute in studies of transition metal complexes because each complex typically has several weak metal–ligand bonds. Waller *et al.*[7] have studied CO vibrational and rotational distributions from Fe(CO)$_5$. In modeling the experimental results, they assumed that the overall CO state distributions arise from sequential loss of up to three CO ligands by an RRKM-type mechanism with statistical partitioning of energy among the photofragments at each step. Thus, the observed distributions do not correspond to a single elementary step but rather to a convolution of processes, making comparison of theory and experiment difficult.

One of the advantages of studying a complex like CpNiNO is that there are only two metal–ligand bonds. Nitric oxide photofragments could, in principle, arise from primary dissociation of CpNiNO or from secondary dissociation of NiNO following loss of Cp. Although we do not have direct evidence for the order of ligand loss from the complex, indirect evidence suggests that secondary loss of NO is a minor process and our observations are at least mainly attributable to primary dissociation of the parent compound.

The first indication that this is true comes from estimates of the bond energies of nickel to Cp and NO. Although the thermochemistry is not known well, typical metal–Cp bond energies are of the order 300 kJ/mol.[17] Metal nitrosyl bonds are typically much weaker, about 200 kJ/mol. The Ni–NO bond energy in $CpNiNO^+$, e.g., is 188 ± 20 kJ/mol.[18] We calculate[19] that if dissociation occurs by an RRKM mechanism, initial loss of NO should be favored by about 1500:1 compared with initial loss of Cp.

Even if a substantial fraction of parent molecules lose Cp first, a statistical partitioning of excess energy would leave the NiNO fragment with insufficient energy to dissociate. The energy of a 225 nm photon exceeds the combined metal-ligand bond energies by only about 70 kJ/mol, so it is unlikely that both ligands can be released without absorbing additional photons. Since we detect only free NO in the experiment, dissociation channels leading to NiNO + Cp would go unobserved.

Further indirect evidence for preferential scission of the Ni–NO bond comes from UV photolysis experiments of CpNiNO isolated in solid matrices.[4] In these experiments the Cp ligand was apparently undisturbed, while the NO ligand was either dissociated or distorted to form a metastable complex.

Finally, electron impact ionization of CpNiNO results in preferential loss of NO to form $CpNi^+$ as the major daughter ion.[20] Very little $NiNO^+$ is observed. In another study, it was shown that photodissociation of $CpNiNO^+$ occurs exclusively by loss of NO.[18]

Overall, we are convinced that the NO fragments observed in our experiment are due to single photon excitation of CpNiNO followed by scission of the Ni–NO bond. While other processes (such as initial loss of Cp) may also occur, they apparently do not lead to production of free NO within 10 ns, the nominal duration of the laser pulse. This greatly simplifies the interpretation of the experimental results since only one primary photochemical process contributes to the observations.

We turn now to the interpretation of the NO rotational state distribution. Qualitatively, our results are inconsistent with a direct dissociation mechanism from a repulsive excited state of the parent molecule. In such a case, dissociation should be rapid compared with rotation of the parent molecule, and we would expect to form NO photofragments with some degree of alignment either parallel or perpendicular to the laser polarization axis. Also, the population ratio of the two spin–orbit states exhibits no unusual behavior which might be indicative of a direct dissociation mechanism. Finally, the rotational distribution expected for an impulsive dissociation mechanism is expected to be distinctly non-Boltzmann in character, as in the case of methyl nitrite.[21]

Two other possible sources of rotational motion in the NO photofragments arise from rotational and bending motion of the parent CpNiNO molecule. Since the nitrosyl ligand is linear and lies along the principal axis of the parent molecule, it is straightforward to calculate that the average rotational excitation in the fragments due to parent rotation is only about 6 cm^{-1}.[22] Consequently, this makes an insignificant contribution to the observed state distributions. In contrast, bending vibrations of the parent molecule may make a much larger contribution. Morse and Freed[23,24] have developed a Franck–Condon model of photodissociation in triatomic molecules in which bending wave functions of the parent molecule are mapped directly onto rotational wave functions of the diatomic fragment. If we treat CpNiNO as a pseudotriatomic molecule in which CpNi is considered to be an atom, then this simple model predicts that the NO photofragment rotational temperature should be 330 K. Although this is a significant effect, the magnitude of the excitation is much too small to completely account for the observed rotational distribution in our experiments.

We turn next to statistical models of photodissociation. We have calculated prior distributions using the information theory approach.[25] This approach has often been used to successfully treat fragmentation in polyatomic molecules. An approximate treatment of state counting[26] which includes energy conservation (but does not explicitly conserve angular momentum) yields Eq. (2) for the predicted NO fragment rotational distribution in the $v = 0$ level

$$N'(J) \propto (2J+1)\,[h\nu - E_0 - E_{\rm rot}(J) + aE_z]^{s + r/2 + 1/2}. \tag{2}$$

The threshold energy E_0 is taken to be the bond dissociation energy of the CpNi–NO bond (200 kJ/mol). The term aE_z is the zero-point energy of the CpNi fragment multiplied by the Whitten–Rabinovitch parameter, a. This is the same term which is frequently used to evaluate sums and densities of vibrational states in RRKM calculations.[26] The nonfixed energy is statistically distributed among s vibrational modes of CpNi ($s = 27$), r rotational degrees of freedom ($r = 3$), and relative translation of the two fragments (which accounts for the extra factor of 1/2 in the exponent). In the calculation of aE_z, we have approximated the vibrational frequencies of CpNi with frequencies and assignments of the parent molecule,[27,28] as given in Table I.

The NO photofragment rotational distribution predicted by Eq. (2) closely approximates a Boltzmann distribution at $T = 2100$ K for $E_{\rm rot} < 2500$ cm^{-1}. This is more than twice as hot as the observed distributions, well outside the uncertainty limits of the experiment. A brief discussion is given in the Appendix concerning the reasons why statistical fragment state distributions from large parent molecules should resemble Boltzmann distributions.

Despite the large difference between theory and experiment, the qualitative aspects of the observed state distributions nevertheless seem to point toward a statistical partitioning of photofragment energies. The rotational and spin–orbit distributions are characterized by a Boltzmann distribution at 900 ± 200 K, there is no evidence of alignment of the photofragments relative to the laser polarization, and there is no preference for generating NO in either lambda-doublet state. Indeed, previous studies[7,8] of ligand fragment distributions from organometallic compounds have, with rare exception,[29] given results consistent with statistical models of energy disposal in the photofragments.

There are several ways in which a statistical calculation can be abused to give agreement with experiment. One is to use the number of oscillators as an adjustable parameter. Sometimes the value of s in Eq. (3) is decreased to suggest

TABLE I. Vibrational frequencies[a] of CpNi used in the RRKM and prior calculations.

Species	Type	$\bar{\nu}$ (cm^{-1})
A_1	C–H stretch	3118
	Ring breathing	1112
	o.p.[c] δ(C–H)	803
	Ring–Ni stretch	315
A_2	i.p.[d] δ(C–H)	1240[b]
E_1	C–H stretch	3105
	C–C stretch	1422
	i.p. δ(C–H)	1005
	i.p. δ(C–H)	1054
	Ring tilt	290[b]
E_2	C–H stretch	3098[b]
	C–C stretch	1340
	o.p. δ(C–H)	1102
	o.p. δ(C–H)	964[b]
	i.p. δ(ring)	841[b]
	o.p. δ(ring)	562

[a] Unless otherwise noted, the frequencies are those of gas phase CpNiNO (Ref. 27).

[b] Frequencies of CpNiNO in solution (Ref. 28).

[c] Out of plane.

[d] In plane.

that the available energy is randomly distributed over a subset of oscillators in the molecule. However, this would not improve the agreement between theory and experiment in our case since it tends to make the calculated distributions hotter, not colder. There is no theoretical justification for increasing the value of *s*.

Recently, the "separate statistical ensembles" method was introduced[30,31] to account for observed rotational distributions[32,33] which are colder than expected from statistical theories. We have made such a calculation for CpNiNO within the context of information theory (without explicit conservation of angular momentum). The predicted NO rotational temperature is decreased by only 100 K from the prediction of Eq. (2).

Another method of manipulating statistical calculations is to change the vibrational frequencies of the fragments. Decreasing all of the frequencies in Table I by 30% results in a decrease in the calculated temperature of only 150 K or 7%. Agreement between theory and experiment would require the vibrational frequencies to be altered by an amount that is unreasonably large.

Finally, a statistical calculation can be altered by raising the threshold energy for dissociation. Physically, this would correspond to the existence of a barrier in the exit channel of the reaction, or perhaps dissociation to an excited electronic state of the fragments. Either case decreases the amount of energy which is available for disposal into fragment vibration. In the case of the exit channel barrier, the amount of energy corresponding to the barrier height is disposed primarily into relative translation and rotation of the fragments as they scatter from the repulsive part of the potential. If dissociation occurs to an excited electronic state of the fragment, the excitation energy is not available to excite translations or rotations of the fragments. The latter explanation is therefore more attractive from the standpoint of rationalizing rotational distributions which are colder than expected.

Following this line of reasoning, we have manipulated Eq. (2) using the value of E_0 as an adjustable parameter. Good agreement with the experimentally determined distributions is obtained when $E_0 = 420$ kJ/mol. This value is about 220 kJ/mol in excess of our estimate for the CpNi–NO bond dissociation energy. One possible interpretation of our experiment, therefore, is that dissociation of CpNiNO produces the CpNi in an excited electronic state lying approximately 220 kJ/mol above the ground state of CpNi.

This interpretation of our experimental results is not unique, of course. We offer it only as one possible model which is consistent with all of our results. Converting E_0 in Eq. (2) to an adjustable parameter pushes the theory of statistical fragment state distributions well beyond its intended limits. In view of the fact that the heat of formation of CpNi is not accurately known (let alone the vibrational frequencies!) we run a calculated risk of overinterpreting our results.

Nevertheless, there is one additional reason to believe that formation of CpNi in an excited state is a reasonable explanation for our results. Rösch *et al.* have recently observed[34,35] luminescence in the visible from an excited state of $Ni(CO)_3$ following UV photodissociation of $Ni(CO)_4$. Therefore, the suggestion that an organometallic fragment might be formed in an excited electronic state is not unprecedented. In fact, within the framework of extended Hückel theory,[36] CpNi and $Ni(CO)_3$ are isolobal (share the same ordering of symmetry-adapted orbitals). The similarity between the electronic structures of the parent molecules and fragments might be responsible for similar photodissociation mechanisms.

CONCLUSIONS

We have obtained [1 + 1] REMPI spectra of NO photofragments following dissociation of CpNiNO near 225 nm using a tunable pulsed laser. The rotational and spin–orbit state distributions determined from the spectra are characterized by a temperature of 900 ± 200 K. The experimental results show that CpNiNO is excited by a single photon prior to dissociation. Furthermore, indirect evidence strongly indicates that the NO is produced by primary dissociation of the parent molecule rather than secondary fragmentation of NiNO. The fact that the fragment distributions are characterized by a temperature suggests that energy partitioning in the fragments is statistical, but the expected distributions based on dissociation to fragments in their electronic ground states are about twice as hot as the observed distributions. A likely explanation for the discrepancy is that the CpNi fragment is produced in an excited electronic state lying about 220 kJ/mol, or 18 000 cm^{-1} above the ground state.

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APPENDIX

Here we consider the reasons why a statistical photofragment state distribution should resemble a Boltzmann distribution. Each molecule is excited with a photon of well-defined energy, so we have a microcanonical ensemble of parent molecules each having the same internal energy (ignoring the relatively small amount of thermal energy present before excitation). At first glance there is no particular reason to expect the fragments of such an ensemble to exhibit temperature-like distributions. Each molecule, however, consists of a finite ensemble of oscillators and rotors which (in the statistical limit) freely exchange the available energy in the molecule. If the number of oscillators is large, then each molecule acts like a canonical ensemble. The rotational motion of the NO fragment arises primarily from a relatively small subset of these oscillators and rotors, and therefore should assume a Boltzmann state distribution in the large molecule limit.

Mathematically, we can show this by appropriate manipulation of Eq. (2). Setting $x = h\nu - E_0 + aE_z$ and $n = s + r/2 + 1/2$ and expanding Eq.(2) in a Taylor series about $E_{\rm rot} = 0$, we obtain Eq. (Al)

$$N'(J) = (2J+1)[1 - nE_{\rm rot}/x + n(n-1) \times (E_{\rm rot}/x)^2/2 - \cdots]. \quad \text{(A1)}$$

We have divided the right-hand side of Eq. (A2) by the constant x^n such that $N'(0) = 1$ for convenience. If we now consider a true Boltzmann distribution and similarly expand it in a Taylor series about $E_{\rm rot} = 0$ we obtain Eq. (A2):

$$N_B(J) = (2J+1)\exp(-E_{\rm rot}/kT) = (2J+1)[1 - E_{\rm rot}/kT + (E_{\rm rot}/kT)^2/2 - \cdots]. \quad \text{(A2)}$$

Note the similarity between the two equations. If we set $x/n = kT$ in Eq. (A1) then the second terms of both equations become identical. The third terms in the expansion differ only by a factor of $(n-1)/n$ (less than 4% for CpNiNO). The fourth terms (not shown) differ by $(n-1)(n-2)/n^2$, and so on.

The statistical and Boltzmann distributions are identical in two limits. First, as the parent molecule becomes infinitely large, $(n-1)/n = 1$ and all of the terms in Eqs. (3) and (4) become identical. Secondly, for molecules of finite size, we may consider only that portion of the fragment state distribution at low energies which satisfy the condition $E_{\rm rot} \ll x/n$. Under these conditions, both series converge rapidly and the overall difference between Eqs. (3) and (4) (due to high order terms) becomes negligible. Therefore, we expect that statistical partitioning of energy within large polyatomic parent molecules should result in fragments which adopt temperature-like state distributions, at least at low energies.

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