J. Am. Chem. Soc. 1996, 118, 7853−7854 7853

Vibrational Relaxation in Metalloporphyrin CO Complexes

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Received May 6, 1996

In order to better understand the relationships between molecular structure and vibrational dynamics, we have investigated the rates of vibrational relaxation (VR) of carbon monoxide bound to the active site of synthetic metalloporphyrin complexes. Here VR is used to denote *vibrational energy relaxation*, the loss of energy from vibrationally excited CO to the rest of the system. VR rates were determined using picosecond mid-infrared (mid-IR) pump−probe experiments.[1,2] In this work, we have investigated a large number of heme complexes and find a *remarkable* correlation between the vibrational lifetime and the carbonyl stretching frequency. By changing the metal atom, the *trans* axial ligand, and the porphyrin substituents, it becomes possible to tune the vibrational relaxation lifetime of CO over about a factor of 4. Never before has virtually continuous control of a vibrational lifetime been observed in a condensed phase polyatomic molecule.

Loss of vibrational energy from CO inherently involves anharmonic coupling between the carbonyl vibrational fundamental and its surroundings.[3] In broad terms, there are three ways this might occur, as illustrated schematically in Figure 1. VR might be a purely intramolecular process, involving CO-to-metalloporphyrin energy transfer via the covalent metalloporphyrin−CO bonds. There are both σ- and π-orbitals involved in M−CO bonding; the π-bonds are formed by backbonding, i.e., back-donation from the metal d_π and porphyrin p_π orbitals to the π^* antibonding orbitals of CO.[4] Alternatively, carbonyl VR might be a purely intermolecular process, involving CO-to-solvent energy transfer via nonbonded interactions. Finally, VR might involve a mixture of intermolecular and intramolecular processes. For example, some of the excess energy might be transferred to porphyrin vibrations and the remainder to low-frequency collective vibrations of the solvent (instantaneous normal modes or solvent phonons).[5]

In order to establish the mechanism of carbonyl VR, we systematically varied the structure of the heme using different metal atoms in an isoelectronic series, different porphyrins (which are the ligands *cis* to the CO), and different *trans* axial ligands. In addition, experiments were performed using different solvents and isotopic substitution with ^{13}CO. We believe that the dominant mechanism of VR involves intramolecular anharmonic coupling from CO to the metalloporphyrin, via the metalloporphyrin−CO π-bonds, rather than the metal−CO σ-bonds. Structural and electronic factors that increase backbonding decrease both ν_{CO} and the VR lifetime by increasing the through π-bond coupling.[6]

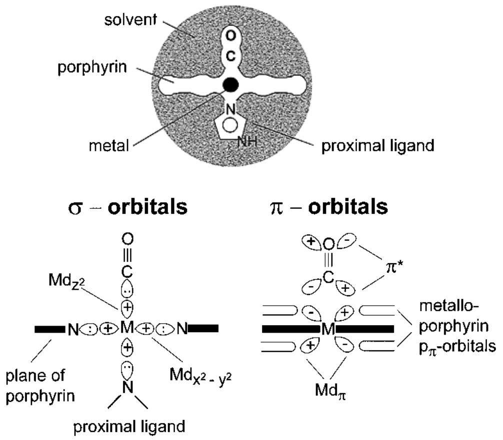

Figure 1. Schematic diagram of CO bound to a metalloporphyrin. Loss of vibrational energy from CO excited by a mid-IR picosecond laser pulse might involve intramolecular CO-to-heme vibration processes, intermolecular CO-to-solvent vibration processes, or a mixed process involving intra- or intermolecular vibrations and solvent phonons. CO-to-heme processes must depend on metal to CO bonding. M−CO bonding involves both σ- and π-orbitals. The M−CO π-bonds are formed by back-donation of electrons from the metal and the macrocycle to antibonding π^* orbitals of CO.

The preparation of the metalloporphyrin complexes followed standard literature methods.[7,8] The pump−probe experiment measures the vibrational lifetime of the CO stretching mode,[1,9] which, for the compounds studied here, lies in the 1980−1880 cm^{-1} range. Pump−probe measurements were performed at the Stanford Free Electron Laser Center, as described in detail elsewhere.[1]

In Figure 2, we plot the VR rate versus carbonyl stretching frequency in CH$_2$Cl$_2$ solutions for M(porph)(CO)(L) for two different porphyrins (TPP and PHDME), three metals (M = Fe, Ru, Os), and five nitrogenous ligands. We observe a very strong correlation between the VR rate and the carbonyl

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[7] (a) Abbreviations: coproporphyrinate-I tetraisopropyl ester, COPRO; 5,10,15,20-tetraphenylporphyrinate, TPP; protoporphyrinate-IX dimethyl ester, PHDME; protoporphyrinate-IX, PPIX. (b) Iron porphyrins and free-base porphyrins were purchased from Aldrich Chemicals. Fe(PHDME)(Cl) and Fe(TPP)(Cl) were dissolved in CH$_2$Cl$_2$, and a 2-fold excess of the appropriate ligand was added. The Fe was reduced with sodium dithionite, and CO was added. The ruthenium and osmium porphyrin carbonyls were synthesized[8] from free-base porphyrins using Ru$_3$(CO)$_{12}$ and Os$_3$(CO)$_{12}$. All compounds used here had a single dominant conformer, as evidenced by a single carbonyl stretch in the FTIR. The ^{13}CO forms were synthesized from the ^{12}CO compounds by irradiation with visible light in the presence of ^{13}CO; complete exchange was confirmed by FTIR.

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[9] (a) All the pump−probe decay data obtained in this study were well fit by a single exponential function of the form $S(t) = S_0 \exp(-t/T_1)$, where T_1 is the lifetime of vibrationally excited ($\upsilon = 1$) metal-bound CO. The error bounds on T_1 are estimated at $\pm(1-2)$ ps and on ν_{CO} at ± 1 cm^{-1}. (b) Heilweil, E. J.; Cavanagh, R. R.; Stephenson, J. C. *J. Chem. Phys.* **1988**, *89*, 230. (c) Tokmakoff, R. S. Urdahl, D. Zimdars, R. S. Frances, A. S. Kwok and M. D. Fayer, J. *Chem. Phys.* **1995**, *102*, 3919.

S0002-7863(96)01494-1 CCC: $12.00

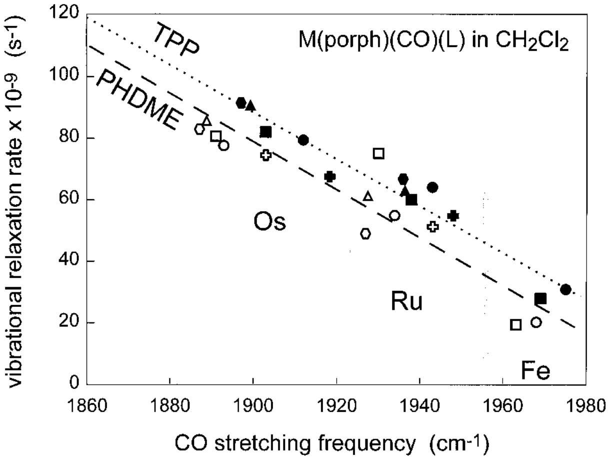

Figure 2. Carbonyl VR rate versus carbonyl stretching frequency ν_{CO} for a series of metalloporphyrin complexes in CH_2Cl_2: (a) M(TPP)(CO)(L) data in solid-filled symbols; (b) M(PHDME)(CO)(L) data in unfilled symbols; L = pyridine (●); 4-aminopyridine (■); 4-cyanopyridine (cross shape); imidazole (▲); 2-methylimidazole (⬢). The dotted and dashed lines are the least-squares fits for each porphyrin, respectively.

stretching frequency, ν_{CO}: VR rates *increase* as ν_{CO} *decreases*. The vibrational lifetimes are quite sensitive to the value of ν_{CO}. Over a range (~1980−1900 cm^{-1}) where ν_{CO} changes by ~4%, the CO vibrational lifetimes range over a factor of ~4 (the longest lifetimes are ~45 ps; the shortest ~11 ps; numerical data are available in the supporting information).[10]

The decrease in VR lifetime with increasing mass of the metal atom is exactly opposite what one expects if through σ-bond coupling were dominant.[6,11] For σ-bond coupling, the CO oscillator loses energy by driving the M−C oscillator. When M is made heavier, the amplitudes of metal oscillations decrease, and the extent of through σ-bond coupling should decrease.[2,6] Thus, a through σ-bond coupling mechanism can be convincingly ruled out.

In order to explore solvent-coupled VR mechanisms, a series of chlorinated hydrocarbon solvents were used. For CCl_4, $CHCl_3$, CH_2Cl_2, and CH_3CCl_3, very little change in the CO VR lifetime is observed for Ru(TPP)(CO)(pyridine). These chemically-similar solvents have relatively weak interactions with our metalloporphyrins, and as a consequence the observed ν_{CO} values do not change significantly. They do differ, however, quite dramatically in the density of solvent vibrational states among the higher frequency molecular vibration region[12] and also to a significant extent in the lower frequency solvent phonon region.[13] There are a great number combinations or overtones of porphyrin vibrational states that can be resonant. In fact, there is sufficient state density near ν_{CO} that an efficient, purely intramolecular[14] CO-to-metalloporphyrin vibration process is possible, requiring little or no involvement of solvent. Because ν_{CO} and the VR lifetime are strongly affected by the structure and electronics of the metalloporphyrin complex, the coupling that matters is CO to metalloporphyrin, rather than CO to solvent.[15] Strongly polar and hydrogen bonding solvents are currently being examined; the potential for specific interactions between solvent molecules and the terminal oxygen atom of bound CO, however, will make interpretation of such data more difficult.

The effects of substituting ^{13}CO for ^{12}CO are especially noteworthy: there is essentially no isotope effect on the VR rate (for M(COPRO)(CO)(pyridine) in CH_2Cl_2 for M = Ru, Os). In spite of a substantial frequency red shift, the pump−probe data are virtually indistinguishable. This rules out the possibility that the lifetime−frequency correlation is due to the structure of the density of vibrational states near ν_{CO}. The isotope effect experiments clearly demonstrate the lifetime−frequency correlation does not depend on the absolute value of ν_{CO}, but instead on the *induced shift* of ν_{CO} caused by changing the chemical structure and thus on the extent of back-bonding.[6]

Our synthetic heme complexes provide new insights into pump−probe experiments on Mb−CO. Limited VR rate data on Mb conformers and mutants suggest the existence of a lifetime−frequency correlation for proteins,[1,6] very similar to that for the synthetic metalloporphyrin complexes. In comparing Mb to PHDME, it is clear the protein VR lifetimes at a given ν_{CO} are noticeably shorter (~20%). Local environment effects appear to be the most likely explanation for the systematically faster VR in proteins, compared to that in PHDME, since the heme structures are nearly identical. It is well known that electrostatic interactions between residues in the heme pocket (*e.g.*, the distal histidine) and heme−CO can account for the different ν_{CO} values in heme proteins.[4cd,16] The question arises whether the protein affects the VR rate simply by affecting the back-bonding and the through π-bond coupling between heme and CO, or whether specific interactions between protein and CO permit CO-to-protein vibrational energy transfer. If specific interactions were responsible for carbonyl VR, then a rather complicated dependence of the VR rate on the details of the protein structure would be expected to result. Instead a very simple, linear lifetime−frequency correlation is observed.[1]

Acknowledgment. This research was supported by ONR (Grants NOOO14-95-1-0259 (D.D.D.) and NOOO14-91-C-0170 (M.D.F.)), NSF (Grants DMR-94-04806 (D.D.D.) and DMR-93-22504 (M.D.F.)), NIH (Grant HL-25934 (K.S.S.)), and NSF fellowship support (C.J.Z.). We thank Professors A. Schwettman and T. Smith and their research groups at the Stanford Free Electron Laser Center for making it possible to perform these experiments. We also acknowledge the assistance of Mr. Michael M. Rosenblatt for his synthesis of the coproporphyrin samples.

Supporting Information Available: Table of vibrational lifetimes and frequencies (2 pages). See any current masthead page for ordering and Internet access instructions.

JA961494W

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(10) In comparing the TPP and PHDME data, the slopes of the best-fit lines through the data are identical to within experimental error, while the intercepts are slightly different. At a given frequency, the VR rates for TPP compounds are on average about 10% faster than for PHDME compounds. This may mean that the phenyl substituents on TPP complexes increase the fluctuating forces on CO responsible for VR, thus increasing the VR rate without affecting ν_{CO}. Alternatively, TPP could affect ν_{CO}, perhaps by changing the M−CO σ-bonding, without significantly increasing the fluctuating forces on CO.

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(15) We have found one solvent, dibutyl phthalate (DBP), that noticeably affects the VR lifetime (11.5 vs 15.6 ps for CH_2Cl_2) without affecting ν_{CO}. DBP is an aromatic ester which may have stronger interactions with the bound CO than the chlorocarbons. DBP also has a much larger density of vibrational states near ν_{CO} and a higher phonon frequency cutoff. These factors tend to increase the likelihood of CO-to-DBP vibrational energy transfer, which may well account for the decrease in vibrational lifetime in DBP compared to CH_2Cl_2.

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