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Tunable infrared picosecond pulses in the 5 μ region have been used for time-resolved pump–probe measurements of the population relaxation lifetime (T_1) of CO($v = 1$) stretching vibrations in a series of metal–carbonyl cluster compounds in room temperature chloroform solution. T_1 was the same for symmetric ($v = 2084$ cm^{-1}, 90 $\pm$ 10 ps) and antisymmetric (2014 cm^{-1}, 87 $\pm$ 10 ps) modes of the dicarbonyl Rh(CO)$_2$(C$_5$H$_7$O$_2$); T_1 was the same for the B_1 (2092 cm^{-1}, 710 $\pm$ 130 ps) and B_2 (2036 cm^{-1}, 750 $\pm$ 90 ps) modes of Rh$_2$(CO)$_4$Cl$_2$. Similarly long T_1 times were found for Rh$_4$(CO)$_{12}$ (2075 cm^{-1}, 610 $\pm$ 65 ps) and Rh$_6$(CO)$_{16}$ (2077 cm^{-1}, 700 $\pm$ 100 ps). The molecule Co$_4$(CO)$_{12}$ has also been compared to the corresponding rhodium analog and it exhibits an initially fast relaxation of 47 $\pm$ 5 ps followed by a slower 396 $\pm$ 70 ps decay. The transient response of the more complex systems to the single frequency experiment is found to be sensitive to frequency and can exhibit bleaching, absorption, and a combination of these effects. Such behavior is attributed to overlap of the IR pulse with $v = 1$ to $v = 2$ and higher transitions in the M$_4$(CO)$_{12}$ (M = Rh or Co) and Rh$_6$(CO)$_{16}$ molecules. The long CO($v = 1$) T_1 values for the metal cluster molecules suggest relaxation via multiquantum transfer of vibrational energy to adjacent M–C stretch and M–C–O bend vibrations; energy transfer to vibrational or electronic states of the central metal core seems unimportant in determining T_1 for these systems.

I. INTRODUCTION

Vibrational energy dynamics have been extensively studied for a wide range of molecular systems and chemical environments over the past several decades. The participation of populated ground electronic state vibrational modes in the rupture of specific chemical bonds during a chemical reaction has fueled much of the interest in this area of research. While many experiments were primarily concerned with gas phase nonradiative and collisional vibrational energy transfer (VET) processes,[1–4] the advent of picosecond lasers and related time-resolved vibrational spectroscopies has extended the earlier methods to a significantly shorter time scale. It is now possible to measure vibrational relaxation rates in the condensed phase at elevated temperatures[5,6] where vibrational relaxation rates are generally found to be greater than 10^9 s^{-1}. Some examples of liquid phase systems that have been studied using picosecond laser techniques include high frequency stretching vibrations such as CH,[6–8] NH,[9] and OH[10] modes of various polyatomic molecules in neat liquid and halogenated-methane room temperature solutions.

It would be particularly informative, however, to measure the T_1 decay of vibrational excitation of adsorbate modes when a molecule is chemically bound to the surface of a metal. Knowledge about this time scale should help clarify how vibrational energy transfer participates in such processes as thermal desorption,[11] surface diffusion,[12,13] laser heating,[14–19] and chemical reaction on catalytic[20–22] or single crystal[23–25] metal surfaces. To date, limits on energy decay times for simple diatomic adsorbates on metals have been solely derived from theoretical estimates[26–30] and comparison to vibrational spectroscopic bandwidth measurements.[30–33] For instance, it has been calculated that an oscillating vibrational dipole can couple its energy extremely rapidly (in less than a few picoseconds) to the electronic degrees of freedom (electron–hole pair excitation) of the metal.[26–30] Bandwidth measurements for CO on transition metal single crystals as a function of temperature have corroborated these estimates,[31–35] but it is difficult to extract an energy or population decay time from a vibrational band which is inhomogeneously broadened and/or dominated by dephasing contributions. It is therefore necessary to perform direct time-resolved measurements of population relaxation in adsorbate–metal systems to compare to theory and frequency-domain techniques.

Metal–carbonyl cluster compounds[36–44] provide an exceptionally rich area for probing vibrational relaxation rates of high frequency CO-stretching modes in chemically active molecules. These systems have also been extensively characterized in terms of their structural,[36–44] spectroscopic,[36,39–41,45] photochemical,[46–48] and catalytic properties.[49–51] The insight gained from these model compounds has frequently provided the basis for understanding more complex chemical systems. For instance, the study of metal cluster compounds has contributed greatly to the basic understanding of the chemistry of technical catalysts[52–56] and reactions on metal single crystals.[52–54] With the eventual goal of measuring T_1 for an adsorbate on a transition metal surface, we initiated a sequence of experiments to directly measure the CO($v = 1$) lifetime for transition metal–carbonyl molecules in solution containing an increasing number of metal atoms and stabilizing CO ligands. Our first measurements, using a single frequency IR bleaching method, were performed on single metal atom containing systems.[57] It was found that T_1 was about 70 ps for M(CO)Cl(TPP)$_3$ (M = Rh, Ir,

TPP = triphenylphosphine) systems in CCl_4 and other organic solvents, while hexacarbonyl systems $M(CO)_6$ (M = Cr,W) gave $400 < T_1 < 700$ ps. These results indicated that M–CO systems have long CO-stretching lifetimes if the molecule lacks ligands with near-resonant accepting vibrational modes.[57]

In this paper, stable inorganic metal–carbonyl cluster molecules in room temperature, dilute solution are examined for the first time. Results for the T_1 lifetimes of terminal CO($v=1$) stretching modes in the systems $Rh(CO)_2(C_5H_7O_2)$ ($C_5H_7O_2$ or 2,4-pentanedionate), $Rh_2(CO)_4Cl_2$, $Rh_4(CO)_{12}$, $Co_4(CO)_{12}$, and $Rh_6(CO)_{16}$ in $CHCl_3$ solution at room temperature are presented. These systems have been used extensively in the past as models for CO adsorbed at specific metal sites (i.e., a-top, bridge and face centered).[58,59] The rich vibrational spectroscopy of these and related species has formed the basis for the assignment of observed IR[60,61] and EELS[62,63] spectroscopic bands for CO groups in metal surface sites of the corresponding symmetry. In addition, many of these compounds exhibit catalytic behavior in a variety of homogeneous and inhomogeneous chemical reactions.[49,52–56] The present study of CO($v=1$) vibrational population relaxation has revealed new phenomena associated with the single frequency pump–probe measurement technique. The results presented here help establish an overall framework for performing and interpreting related studies of CO adsorbed on supported metal particle catalysts and well-characterized single crystal metal surfaces.

The CO($v=1$) relaxation rates in these metal cluster molecules are found to be long ($> 10^4$ vibrational periods) and not correlated with the total density of molecular vibrational states at the CO-stretching mode energy. The same two results were found earlier for the relaxation of OH ($v=1$) and OD ($v=1$) stretching vibrations for silanol (R_3SiOH) molecules in solution,[10] for the relaxation of OH($v=1$) and OD($v=1$) on silica surfaces,[64,65] and for CO($v=1$) modes for the monometal carbonyls.[57] It is likely that in the metal cluster compounds, as in the hydroxyl systems,[10,64–66] relaxation of the CO($v=1$) modes involves multiquantum (multiphonon) transfer of vibrational energy to modes involving adjacent bonds (i.e., M–C stretches and MCO bends); energy transfer neither to vibrational nor electronic degrees of freedom of the central metal core seems to be important in determining T_1 for the CO($v=1$) stretches of these cluster molecules.

II. EXPERIMENTAL

The method for measuring T_1 is identical to that used in our previous studies of OH($v=1$)[10] and CO($v=1$)[57] systems. Briefly, an intense IR pulse (ν_{IR}) tuned to the $v=0\to1$ transition of a molecular vibrational mode (frequency ν_0) transiently populates the $v=1$ level, partially saturating the $v=0\to1$ absorption. In a pure two-level situation, the excited state population relaxes exponentially with time and the transmission T of a weaker IR probe pulse (same ν_{IR}), delayed in time with respect to the pumping pulse, monitors the difference between the ground ($v=0$) and excited ($v=1$) populations. The quantity $S(t_d)$ $= \ln(T/T_0)$ as a function of delay time t_d (T_0 is the Beer's Law sample transmission) decays as $S(t_d) = S(t_d = 0)$ $\times \exp(-t_d/T_1)$ and gives the $v=1$ excited state T_1 lifetime (T_1^{-1} is the energy decay rate).

For the present study of the terminal, high frequency (2000–2100 cm^{-1}) CO-stretching vibrations in metal cluster compounds, generation of tunable picosecond IR pulses in the 5 μ region has been accomplished by nonlinear difference-frequency generation using a $LiIO_3$ crystal.[67] A 10 Hz active–passive modelocked Nd^{+3}:YAG laser creates 32 ps pulses at 532 nm. A synchronously pumped tunable dye laser produces pulses in the 600 nm region. Mixing the red and green pulses in $LiIO_3$ produces tunable IR pulses with 18 ps FWHM duration, 4 cm^{-1} FWHM bandwidth, and $\sim 15\,\mu$J of energy. IR pulse durations were measured by sum-frequency generation in a second $LiIO_3$ crystal to obtain the two pulse autocorrelation function. A more detailed account of the IR pulse generation technique, the experimental set-up, and the data collection and analysis methods to measure T_1 may be found in an earlier paper.[57]

Solutions of the metal–carbonyl cluster molecules in $CHCl_3$ were freshly prepared by direct dissolution of the solid (as received from the manufacturer) in dried and distilled spectrograde $CHCl_3$ (Mallinkcrodt).[68] $Rh(CO)_2(C_5H_7O_2)$, $Rh_2(CO)_4Cl_2$, and $Rh_6(CO)_{16}$ were obtained from Alpha Chemical Company while $Rh_4(CO)_{12}$ and $Co_4(CO)_{12}$ came from Johnson–Matthey Company. Attempts to study the $Ir_4(CO)_{12}$ analog were unsuccessful because of the low solubility of this molecule in both $CHCl_3$ and CCl_4 solvents.

It was discovered that the 1% by weight ethanol preservative used in $CHCl_3$ affected the T_1 measurement for the larger $Rh_6(CO)_{16}$ cluster compound (reducing the lifetime by a factor of 3). Thus, the solvent was dried for several days over baked 10 Å molecular sieves (Fisher), vacuum distilled to remove the ethanol and then used for all solution preparation. This procedure completely eliminated the ethanol OH absorption feature in the 3620 cm^{-1} region of the IR spectrum. The dried solvent was subsequently stored under vacuum in the dark to prevent decomposition by light and air.

Concentrations of the metal–carbonyls in chloroform were within the range 1×10^{-5} to 1×10^{-4} mole fraction (i.e., less than 2×10^{-3} molar) to obtain peak transmissions (using a stainless steel cell with two sapphire windows separated by a $l = 0.82$ mm Teflon spacer) of between 30% and 60%. A similar cell filled with the same solution was placed in front of the pulse energy-monitoring InSb detector. This cell helped to reduce noise in the probe transmission ratio measurement associated with shot-to-shot fluctuations in pulse frequency. This approach was found to be necessary when ν_{IR} was tuned to the sharply rising band edges during frequency-dependent measurements (see below).

Absorption spectra for the molecules studied are presented in Fig. 1. These solvent and cell-compensated spectra were obtained on an Analect RFX-65 FTIR spectrometer[68] at 0.5 cm^{-1} resolution by subtracting a previously obtained
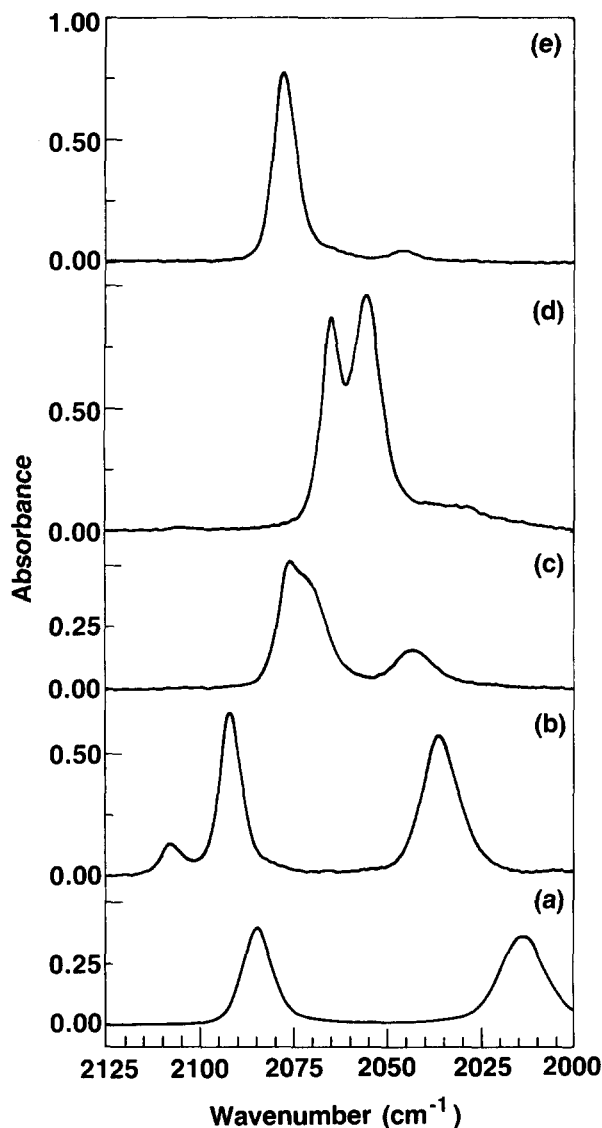
FIG. 1. Absorption spectra of (a) $Rh(CO)_2(C_5H_7O_2)$, 2.1×10^{-3} M; (b) $Rh_2(CO)_4Cl_2$, 1.5×10^{-3} M; (c) $Rh_4(CO)_{12}$, 4.8×10^{-4} M; (d) Co_4 $(CO)_{12}$, 7.9×10^{-4} M; and (e) $Rh_6(CO)_{16}$, 2.5×10^{-4} M in doubly distilled, dried $CHCl_3$ solvent at 295 K. These spectra were obtained at 0.5 wave number (cm^{-1}) resolution in a 0.82 mm pathlength cell after solvent spectrum subtraction. Absorbance is defined as $-\log_{10}(T)$.

FIG. 2. Representative $v = 0 \rightarrow 2$ absorption spectra of $Rh_2(CO)_4Cl_2$ and $Rh_4(CO)_{12}$ in saturated CCl_4 solution at 295 K. Overtone and combination assignments are made for $Rh_2(CO)_4Cl_2$ using mode labels from Ref. 45. The arrows indicate twice the v_{IR} pulse frequency used for the T_1 measurements listed in Table I.

spectrum of the solvent in the same sample cell. This sample cell filled with $CHCl_3$ was 75% transmissive in the CO-stretching region of the spectrum. Solvent absorption or potential thermal lensing effects did not interfere with the T_1 measurements. For comparison purposes, spectra obtained in a similar way for $Rh_2(CO)_4Cl_2$ and $Rh_4(CO)_{12}$ in saturated CCl_4 solution are shown for the $v = 0 \rightarrow 2$ absorption region in Fig. 2. As one can see, the bandwidths for most of the strong IR allowed fundamental vibrations fall in the 8–15 cm^{-1} FWHM range. The combination and overtone region of the spectrum, while relatively straightforward to analyze for the dirhodium compound, is congested for the more complex species. However, the combination mode bandwidths are also found to be about 10–20 cm^{-1} FWHM. The fundamental IR absorption spectra agree well with those available in the literature.[45,69–71]
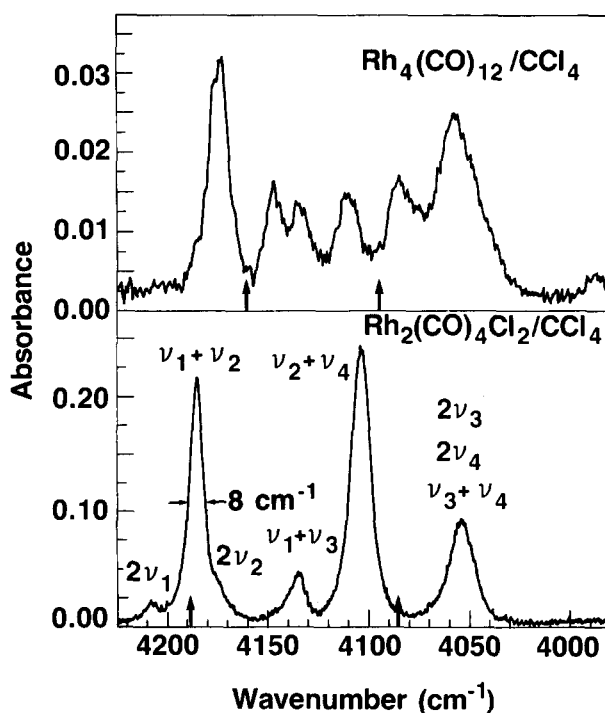
The structures, vibrational assignments, and chemical properties of many of the metal–carbonyl cluster compounds are documented in the literature.[36–45] Mode assignments for the chlorine-bridged $Rh_2(CO)_4Cl_2$ molecule have been made for this geminal -$Rh(CO)_2$ species.[45,46,72,73] The C_{3v} trigonal base with apical metal atom structure of the $M_4(CO)_{12}$ (M = Rh,Co) systems supports two terminal CO groups coordinated to each basal metal atom, three at the apex, and three bridge-bonded CO groups between the basal metal atoms.[69,70,78] Vibrational assignments for the terminal CO-stretching modes were made by Bor et al.[69] while metal–metal modes have been studied using Raman spectroscopy.[74–77] $Rh_6(CO)_{16}$ has an octahedral metal structure with two terminal CO ligands at each Rh atom and four triply coordinated CO groups attached to the octahedral "faces."[78] It takes roughly 30 kcal/mol (1.22×10^4 cm^{-1}) to remove a CO group from a transition metal carbonyl,[79] but NMR studies on $M_4(CO)_{12}$ molecules show that at temperatures above ~230 K, the carbonyls slowly migrate around the metal nucleus by bridge site–apical site isomerization.[80–82] These NMR results also indicate that carbonyl rearrangement occurs on the millisecond or longer time scale at room temperature.

As was discussed in detail in our previous report of monometal carbonyl relaxation,[57] studies of these cluster compounds are facilitated by the large CO-stretching transition dipole moment for transition metal carbonyl ligands

(typical peak absorption cross sections are ~ 0.1–1.5 Å^2 per molecule). This makes it possible to use both extremely low solution concentrations and pulse energies to produce large transmission changes ($\Delta T/T_0 \leqslant 0.6$) in the experiment. Excitation to $v = 2$ and higher lying vibrational levels becomes possible in these systems (see Secs. III B and IV D) because of their small CO-stretching overtone and cross anharmonicities (~ 4–28 cm^{-1} frequency differences).[83-87] However, when tuned to the high frequency side of most CO-stretching fundamentals, the laser pumps only the $v = 0$ to $v = 1$ transition. This permits measurement of T_1 for particular CO($v = 1$) stretching modes by using about 0.05 to 1.0 μJ of IR pump energy (at a fluence of < 10 mJ/cm^2) for the pumping pulse.

Since it is possible for the pumping pulse bandwidth to overlap with $v = 1 \rightarrow 2$ and higher vibrational transitions, multiple up-pumping of a single molecule must be monitored as a function of ν_{IR}. A determination of the number of photons absorbed per molecule was made by measuring the transmission of the pump pulse through the cell. From this value, and knowledge of the energy per pump pulse, the absolute energy absorbed by the sample could be obtained by subtracting the energy absorbed and reflected by the solvent-filled cell ($\sim 75\%$). From measurements of the pump beam radius (w_0 beam radius of 0.0072 cm) and known sample concentrations (ρ = solute molecules per cm^3 of solution), it was then possible to compute the number of photons absorbed per solute molecule, n. Specifically, n = (photons absorbed by sample)/($\pi w_0^2 I \rho/2$), should be below 0.5 in order for the saturation decay rate to be easily interpreted in terms of T_1 for a CO($v = 1$) level.

III. RESULTS

A. Measured T_1 decays and lifetimes

Examples of the types of transient signals obtained as a function of probe delay time t_d and plotted semilogarithmically for single experimental runs are shown in Figs. 3 and 4. In Fig. 3, a transient bleaching decay for Rh$_2$(CO)$_4$Cl$_2$ taken for the 2036 cm^{-1} B_2 antisymmetric CO stretch is presented. For this mode, as well as for the higher frequency B_1 symmetric CO-stretching mode at 2094 cm^{-1}, single exponential decays with $T_1 \approx 730$ ps are obtained. In both cases the number of photons absorbed per molecule is found to be less than 0.5 and this value for T_1 is independent of frequency.

The transient decay signal for the $\nu_0 = 2055$ cm^{-1} vibration (E-type symmetry) of Co$_4$(CO)$_{12}$ is presented in Fig. 4. This is the first biexponential decay observed for any system studied using this IR pump–probe method. In the figure, the signal-to-noise ratio is large enough to be able to extract the contribution of the initially fast decay component from the slower one. By extrapolating the long time-constant ($T_1 = 390$ ps) decay back to time $t_d = 0$, one obtains the short-time relaxation behavior by direct subtraction (see Fig. 4). A lifetime of 47 ps is deduced for the shorter relaxation event. Many similar runs made on the same system, as a function of frequency (both 2055 and 2065 cm^{-1} features showed similar fast and slow decay components) and power, yielded decays with the ratio of the peak signal to the ex-
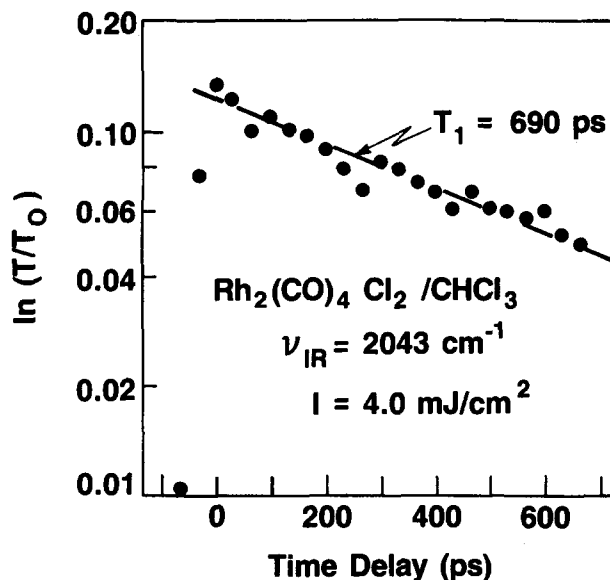

FIG. 3. Transient population decay for the antisymmetric (B_2) CO($v = 1$) stretching fundamental ($\nu_0 = 2036$ cm^{-1}) of Rh$_2$(CO)$_4$Cl$_2$ in dry CHCl$_3$ at room temperature. The $T_1 = 690$ ps indicated relaxation time is for this representative data only (photons absorbed per solute molecule $n = 0.4$).

trapolated long-time decay value at $t_d = 0$ always being about 1.3.

As is evident in these figures, the signal $\ln(T/T_0)$ decays with a time constant that is much longer than the measured IR pulse autocorrelation of 25 ps FWHM. This makes extraction of the relevant T_1 lifetimes relatively straightforward. The values for T_1 were all found to fall in the hundreds of picoseconds time regime [except for Rh(CO)$_2$(C$_5$H$_7$O$_2$) and the fast component of Co$_4$(CO)$_{12}$] which corresponds to population relaxation in about 4×10^4 vibrational periods.

A compilation of the T_1 lifetimes for the metal–carbonyl cluster compounds studied in this work is summarized in Table I. In this table, we present the various systems examined, their peak absorption frequencies (ν_0), cross sec-
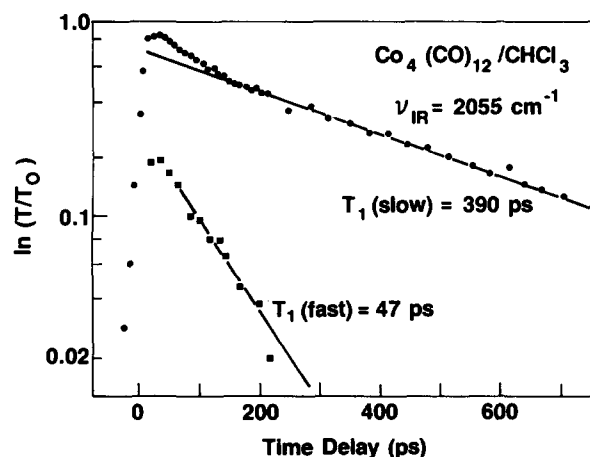

FIG. 4. CO($v = 1$) transient decay for the E-symmetry stretching mode of Co$_4$(CO)$_{12}$ at 2055 cm^{-1} in CHCl$_3$ at 295 K. The T_1 (fast) = 47 ps (lower left) contribution to the decay was obtained by subtracting the experimental points from the extrapolated line of the T_1 (slow) = 390 ps relaxation component.

TABLE I. Complilation of T_1 lifetimes (ps) for CO ($v = 1$) stretching vibrations of metal–carbonyl systems in dilute $CHCl_3$ solution at 295 K. Peak mode frequencies (ν_0), absorption bandwidths ($\Delta\nu$, FWHM), and IR pulse frequencies (ν_{IR}) are in wave numbers (cm^{-1}). I is the pump laser fluence. The peak absorption cross section σ is defined as $\ln(T) = -\rho\sigma l$. n is the average number of pump laser photons absorbed per molecule. The recommended values of T_1 are for conditions that the pump and probe pulses interacted only with the indicated fundamental. References are to structure and spectroscopy for that molecule.

System	ν_0	$\Delta\nu$	σ(Å^2)	ν_{IR}	I^a	n	T_1 (ps)	Rec. T_1	Refs.
Rh(CO)$_2$(C$_5$H$_7$O$_2$)	2084	10	0.085	2084	16	0.1	90	90 ± 11	83,84
	2014	15	0.076	2014	23	$\cdots$	87	87 ± 10	
Rh$_2$(CO)$_4$Cl$_2$	2092	8	0.198	2094	3.7	0.6	687	708 ± 130	45,46,
									72,73
	2036	13	0.170	2043	4.0	0.4	690	750 ± 86	
				2036	13	$\cdots$	733		
Rh$_4$(CO)$_{12}$	2075	b	0.493	2080	2.4	0.5	657	612 ± 63	36,69,
				2074	6.0	1.8	387		70,74,
									76,78
	2043	c	0.177	2047	43	8.0	1000	$\cdots$	
				2042	13	$\cdots$	840		
Co$_4$(CO)$_{12}$	2065	≈8	0.504	2068	1.3	0.3	460	396 ± 67	69,70,
				2066	6.5	0.3	373		74,75,
				2065	6.0	2.0	467		78
	2055	≈12	0.564	2056	8.0	2.0	263	$\cdots$	
				2056	13	$\cdots$	140		
Rh$_6$(CO)$_{16}$	2077	8	1.453	2085	10	2.0	613	698 ± 98	36,43,
				2082	0.8	0.6	720		58,71
				2076	240	21	240		
				2074	10	6.0	d		

$^a I$ in units of mJ/cm^2.
^{b}Overlapping band composed of ν_2 and ν_4 modes.
^{c}Overlapping band composed of ν_3 and ν_5 modes.
^{d}100 ps bleach recovery followed by long time absorption shown in Fig. 5.

tion σ and bandwidths for the modes studied for these molecules, and the laser pulse frequencies ν_{IR} and IR intensities used to perform the measurement. Also included in the table are values for n (the average number of photons absorbed per molecule) and T_1 showing the variation in these quantities as a function of selected IR pulse frequencies and powers. The "recommended T_1" value reported in Table I is the average value (with error limit ± 1σ or ± 10%, whichever is larger) of many runs made for that mode. This value was deduced from runs where ν_{IR} was tuned to the high frequency side of the absorption band, the transient decay was independent of pump pulse intensity, and n was determined to fall below 0.5.

B. Effect of frequency detuning on transient measurements

For situations when the IR pulse is tuned either to the peak (ν_0) or lower frequency side of an absorption band, variations in the observed decay constant and large values of n were obtained with even small changes in ν_{IR}. This effect was especially pronounced for studies of the lower frequency ν_4 component of the ν_2, ν_4 overlapping doublet bands of Rh$_4$(CO)$_{12}$ and Co$_4$(CO)$_{12}$,[69] the ν_3, ν_5 doublet of Rh$_4$(CO)$_{12}$ and the strong absorption band of Rh$_6$(CO)$_{16}$ ($\nu_0 = 2077$ cm^{-1} corresponding to the symmetric stretch of two terminal CO ligands attached to each Rh).[71] As an example of this effect, the transient response [plotting
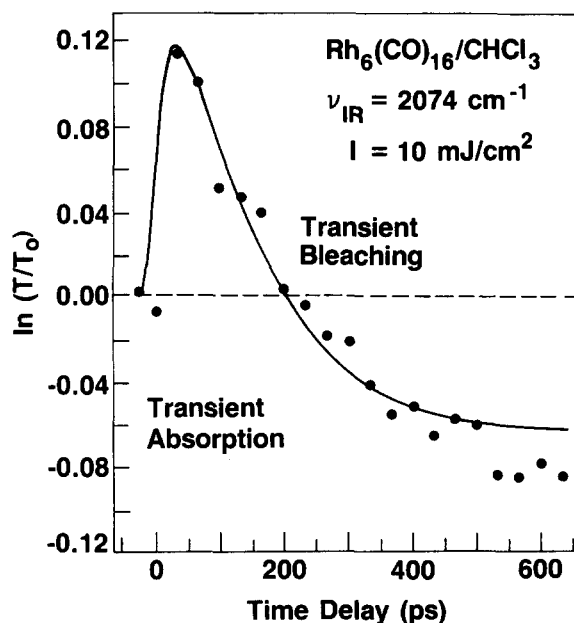
FIG. 5. Transient response for Rh$_6$(CO)$_{16}$ in dry CHCl$_3$ at 295 K. Measured changes in transmission are displayed on a linear scale in order to differentiate transient bleaching (top half) from transient absorption (lower half). With ν_{IR} detuned by 3 cm^{-1} to lower energy from the absorption maximum, an initial bleaching signal is followed by a transient absorption. The solid curve is the result of a computed simulation of the experimental (dotted) data points. A detailed description of the model (see the Appendix) and the parameters used for this simulation may be found in the text.

$\ln(T/T_0)$ linearly] for the $Rh_6(CO)_{16}$ molecule measured at $\nu_{IR} = 2074$ cm^{-1} is depicted in Fig. 5. This figure shows that a *bleaching* signal is first produced near $t_d = 0$ which decays rapidly and then reverts to an *absorption* signal. It is clear that under these conditions, one is no longer able to extract a simple T_1 decay constant for the $v = 1$ level. Evidence for excited state absorption accompanied this transient response since n was found to be greater than 1 [for $Rh_6(CO)_{16}$, values of $n > 20$ were observed]. A more detailed discussion concerning the qualitative agreement between multilevel population flow caused by laser detuning and these results are presented in Sec. IV D and the Appendix.

IV. DISCUSSION

A. Comparison of results to monometal carbonyl systems

For all five molecules presented in Table I, the CO($v = 1$) modes which are probed involve nuclear motion of two CO groups locally bound to the same metal atom [e.g., an equatorial and axial CO for $M_4(CO)_{12}$]. The two CO stretches of $Rh(CO)_2(C_5H_7O_2)$ relax with the same rate constant (1.1×10^{10} s^{-1}), which is seven or eight times faster than rates in the other molecules. Perhaps the frequencies associated with the two carbonyl groups of the 2,4-pentanedionate ligand ($\nu = 1553$, 1513 cm^{-1})[83,84] which are directly bound to the Rh atom are particularly well suited as acceptors of vibrational energy that is initially deposited in the -$Rh(CO)_2$ portion of this molecule.

Except for $Rh(CO)_2(C_5H_7O_2)$, the non-CO-stretching modes of these molecules are at very low frequencies.[74–77,85] As is found in the $M(CO)_6$ systems,[85] the next highest vibrational modes in energy (below the CO-stretching vibrations) are the ν_{MC} metal–carbon stretch and δ_{MCO} metal–carbonyl bending motions, which have frequencies of roughly 450 and 550 cm^{-1}, respectively, for CO bound to metal–hexacarbonyls[85–88] and $Rh_2(CO)_4Cl_2$.[89] Metal–metal vibrations are found to be somewhat lower in frequency (110–220 cm^{-1}).[74–77,85–89] Therefore, conservation of energy requires a minimum of four quanta to be produced in overtones or combinations of these lower frequency modes upon deexcitation of CO($v = 1$). This corresponds to a $V = 5$ decay process, as was defined in our earlier work on OH($v = 1$) relaxation.[10] A decay process involving the simultaneous creation of 4 or more lower-energy quanta is usually a slow one, and as was similarly found for silanol OH($v = 1$)[10] and $M(CO)_6$[57] systems, CO($v = 1$) relaxation in the current systems is also found to be exceedingly long (taking several hundred picoseconds). Thus, for the cluster compounds, we find that they exhibit purely ground electronic state molecular-like behavior with no indication of relaxation to other internal electronic degrees of freedom. For CO on a metal surface, or bound to a sufficiently large metal cluster, a qualitatively new damping mechanism involving energy transfer to low lying electronic states of the metal (electron–hole pair excitation) is possible.[26–29,90,91] This mechanism is thought to dominate vibrational relaxation on metal surfaces, causing T_1 to be a few picoseconds or

less[26,27] and giving rise to the broad (several cm^{-1}) infrared bandwidths observed for many adsorbates.[30–34] However, the long T_1 lifetimes of ~ 700 ps for the small cluster compounds in Table I apparently represent CO ($v = 1$) relaxation only by intramolecular vibrational energy redistribution processes.

B. Coupling between CO ligands

One question concerning vibrational energy decay in cluster compounds of increasing metal nucleus size and carbonyl number is the extent to which CO-stretching vibrations are coupled to one another. Unfortunately, since our present experiments generally show single exponential decays, little information can be deduced about intermode energy transfer in these systems. It is conceivable that some CO-stretching modes of a particular system are coupled to each other on a very fast ($\leqslant$ pulse duration) time scale. The population decay which we observe may be the time for energy transfer from these coupled states to lower frequency modes (i.e., ν_{MC} stretches or δ_{MCO} bends). T_1 is the same (~ 90 ps) for both CO($v = 1$) modes of $Rh(CO)_2(C_5H_7O_2)$ and T_1 is the same (~ 730 ps) for both the B_1 and B_2 symmetry modes of $Rh_2(CO)_4Cl_2$. If these CO-stretching modes were rapidly coupled, then they would necessarily give the same T_1 time in our experiments, as observed. Alternatively, the different CO vibrations may relax independently, with similar couplings to the lower frequency modes, thus resulting in similar T_1 lifetimes. The biexponential decay for the $Co_4(CO)_{12}$ system may indicate that intermode vibrational coupling exists and is measurable in these systems. Unfortunately we cannot uniquely assign the observed fast decay ($T_1 = 50$ ps) to a particular VET process. The two strong absorption bands of $Co_4(CO)_{12}$ at 2055 and 2066 cm^{-1} have been assigned as being of E and A_1 symmetry, respectively.[69] Perhaps because of their different symmetries, coupling of these or other modes occurs on a long enough time scale (~ 50 ps) that we are able to distinguish their population equilibration from their combined longer (~ 350 ps) overall relaxation time. Again, we expect that the coupled population of the CO-stretching modes relaxes predominantly into the lower frequency ν_{MC} and δ_{MCO} modes.[92]

As the symmetry of the molecule becomes higher [i.e., C_{3v} for the $M_4(CO)_{12}$ molecules and T_d for $Rh_6(CO)_{16}$], the IR spectrum can either become more complex [$M_4(CO)_{12}$ showing its six normal mode CO stretches with two very strong bands] or even simpler [$Rh_6(CO)_{16}$ terminal carbonyls exhibiting only one very intense and a second very weak feature]. With ever increasing metal cluster size it becomes necessary to reduce the problem of normal mode assignments to consider only the *local* symmetry of CO groups bound to specific metal atom sites (i.e., axial, equatorial, apical, edge-bridged, or trigonal face-centered sites). Such an approach has frequently been used to make band assignments for CO vibrations adsorbed on metal crystals[58–61] and on supported metal particles.[52,93] It was also the picture used when considering both spectroscopic and T_1 data for OH chemisorbed on the surface of 200 Å diameter silica spheres[66] or OH-containing R_3SiOH silanol mole-

cules.[10] With this in mind, one may hypothesize that the local structure of an adsorbed CO group in a particular environment is the most important characteristic which determines the CO($v = 1$) T_1 lifetime. For the systems studied here, the predominant local structural characteristic is two CO groups attached to a single metal atom (see Refs. 45, 69, and 78 for structures). It is therefore possible that the measured T_1 values are characteristic of the relaxation of the symmetric mode of these terminal CO (local C_{2v} symmetry) groups. That T_1 is sensitive to local molecular structure, which is similar for the metal cluster compounds, may explain why these compounds have nominally the same relaxation lifetime.

T_1 does not depend on the total density of molecular vibrational states, $\rho(E_v)$, for the systems examined here. The molecules which give rise to the transient bleaching in our experiments have an average vibrational energy equal to the pump photon energy plus their room temperature thermal energy: $E_v = E_{thermal} + E_{photon}$. For Rh$_2(CO)_4Cl_2$, E_v(cm^{-1}) $= 2535 + 2094 = 4629$ cm^{-1} and $\rho(E_v) \sim 10^{11}$ states/cm^{-1}. For Rh$_4$(CO)$_{12}$ and Rh$_6$(CO)$_{16}$ one finds $E_v = 6114 + 2079 = 8193$ cm^{-1} and $\rho(E_v) \sim 10^{26}$ states/cm^{-1}, and $E_v = 8040 + 2080 = 10\,120$ cm^{-1} and $\rho(E_v) \sim 10^{36}$ states/cm^{-1}, respectively. For such enormous $\rho(E_v)$, and particularly in solution, the relaxation rate is not constrained by the availability of energetically accessible final states. Rather, T_1 is presumably determined by the strength of the coupling to specific local acceptor modes (i.e., δ_{MCO} bends or ν_{MC} stretches).

C. Intramolecular vibrational relaxation (IVR) and solvent effects

A related question is whether the T_1 lifetimes we measure arise from intramolecular vibrational energy transfer processes (IVR) or are solvent mediated. The total relaxation rate may be written as a combination of these contributions: $k_1 = k_{IVR} + k(solvent) = T_1^{-1}$. In this work we report results for measurements of cluster systems in CHCl$_3$ solvent. One measurement was made of the relaxation of Rh$_2$(CO)$_4$Cl$_2$ ($\nu_0 = 2036$ cm^{-1}) in CCl$_4$ where it was found that T_1 was the same as in CHCl$_3$ solution. Since it seems very unlikely that V–V transfer from the excited CO($v = 1$) mode to the lower frequency solvent modes (e.g., < 750 cm^{-1} for CCl$_4$) would occur more rapidly than energy transfer to other modes within the carbonyl molecule, we believe that in this case energy transfer to the solvent is a minor contribution. However, solvent collisions, which occur at a rate of about 10^{13} s^{-1}, may increase the rate at which vibrational energy relaxes within some metal carbonyl molecules.

Until related measurements of T_1 for the same systems under isolated gas-phase conditions are performed, it will be hard to unambiguously determine k_{IVR} for these systems. We have recently measured the T_1 lifetime of the F_{1u} CO($v = 1$) stretching mode of Cr(CO)$_6$ in the gas phase at $T = 50\,°C$ and obtained the collisionless lifetime $T_1 = 760$ ps.[94] This value is somewhat longer than the $T_1 = 440$ ps lifetime for Cr(CO)$_6$ in room temperature CCl$_4$.[57] It seems that for Cr(CO)$_6$, k_{IVR} and k(solvent) may have similar

contributions to T_1^{-1}. We are now measuring T_1 for a series of gas phase metal carbonyls with appropriately high vapor pressures [e.g., Co(CO)$_3$NO, Co(CO)$_2$(C$_5$H$_5$), Fe(CO)$_3$(C$_4$H$_6$), Mn(CO)$_3$(C$_5$H$_4$CH$_3$), Fe(CO)$_5$] in order to separate the solvent-induced and collisionless IVR contributions to the overall vibrational population relaxation rate.

D. Anomalous transient behavior from frequency detuning

Experimental conditions were found during these studies which produced unexpected transient signals. These include, e.g., the appearance of either transient bleaching, absorption or a mixture of these effects in the same measurement. An example of such a complicated saturation profile is shown in Fig. 5 where data for Rh$_6$(CO)$_{16}$ (see Table I) are plotted. The laser at $\nu_{IR} = 2074$ cm^{-1} was detuned by 3 cm^{-1} from the $\nu_0 = 2077$ cm^{-1} absorption maximum, and despite the low pump pulse energy (1 μJ), an average of $n = 6$ photons were absorbed per Rh$_6$(CO)$_{16}$ molecule in the beam. At first, a transient bleach ($T/T_0 > 1$) is observed which decays in about 170 ps and is followed by a transient absorption ($T/T_0 < 1$) lasting for at least several hundred ps. Also shown in Fig. 5 is T/T_0 calculated by a computer model described in the Appendix; the simulation signal amplitude was multiplied by a scale factor to make the maximum bleaching signal the same size as the experiment.

The computer model gives the following physical basis for the bleach followed by absorption signals. Since the anharmonicity of the CO-stretching mode is small and the integrated intensity of the $i \rightarrow i + 1$ transition increases as $i + 1$, the laser is able to pump the (slightly red-shifted) $v = 2$ and higher modes resulting in their being significantly populated. The absorption associated with the $i \rightarrow i + 1$ transition is proportional to the $N_i - N_{i+1}$ population difference. These population differences are all small following the laser excitation and this results in a transient bleaching signal. The populations in the higher levels then rapidly relax back to the long-lived $v = 1$ bottleneck level, for which we measured (see Table I) $T_1 = 700$ ps. In order to fit the observed time dependence we chose $T_1 = 700$ ps for $v = 1$, 200 ps for $v = 2$, and 40 ps for all higher levels. The absorption for $t_d > 170$ ps occurs because population from higher levels accumulates in the $v = 1$ level and the $1 \rightarrow 2$ absorption cross section at the laser frequency is slightly greater than for the $0 \rightarrow 1$ transition. On a still longer time scale the $v = 1$ level relaxes entirely to the $v = 0$ level and the transient absorption eventually disappears. We note that the T_1 values quoted for the higher levels are simply one set of numbers which roughly fit the data and are not to be taken as recommended T_1 values since it is likely that many combinations of parameters would also fit the data.

There are several conclusions to be drawn from Fig. 5 and other experimental and computer runs. One may see pure bleaching, pure absorption, or various transient combinations for these carbonyl systems, simply by changing the frequency of the laser by a few wave numbers. One may also observe transient bleaching in which the apparent T_1 time depends strongly on laser frequency and intensity. None of

these effects were observed in our previous studies of T_1 for OH, OD, or NH stretching vibrations (where the anharmonicities are $\geqslant 100$ cm^{-1}).[10] However, experiments on carbonyl systems will correctly give T_1 for the $v = 1$ level if two criteria are met: (1) the laser is tuned higher in frequency than the $v = 0 \rightarrow 1$ absorption maximum and (2) n is less than 0.5.

In general, when using ultrashort IR laser pulses to directly populate a vibrational mode with small anharmonicity, one must deliberately tailor the pulse bandwidth and intensity to avoid multiple pumping processes. For the studies presented here, the 4 cm^{-1} FWHM IR pulse bandwidth was adequate for tuning across the 10–15 cm^{-1} FWHM spectral features. Deliberate high-frequency tuning of the pulse also avoided overlap with overtone and combination mode absorption. The ramification of this final comment is that future T_1 measurements of more rapidly relaxing vibrations (subpicosecond) may be difficult to perform using femtosecond IR pulses (or even pulses shorter than a few picoseconds) because the pulse bandwidth ($\Delta\nu_{IR} \geqslant 10$ cm^{-1} FWHM for pulses $\leqslant 1$ ps FWHM) will not necessarily meet the above frequency overlap and photon absorption criteria for some vibrations.

V. CONCLUSIONS

Measurements of T_1 vibrational lifetimes for terminal CO($v = 1$) stretching modes of metal–carbonyl cluster compounds in solution have been made for the first time. For systems which have otherwise only low frequency ($\nu \leqslant 600$ cm^{-1}) vibrational modes that can accept the CO($v = 1$) excitation, metal–carbonyls are found to exhibit extremely long lifetimes. For the Rh–CO series $Rh_2(CO)_4Cl_2$, $Rh_4(CO)_{12}$, and $Rh_6(CO)_{16}$ in dilute, room temperature CHCl$_3$ solution, T_1 was found to be between 600 and 750 ps for the CO-stretching modes. This lifetime corresponds to $\sim 4 \times 10^4$ vibrational periods of the oscillating CO ligand before it loses its excitation. Faster relaxation ($T_1 = 90$ ps) in $Rh(CO)_2(C_5H_7O_2)$ may indicate that nearly resonant energy transfer occurs to the CO-stretching modes of the 2,4-pentanedionate ligand. As was also observed for OH($v = 1$),[10,64–66] these long relaxation lifetimes are not reflected in the simple IR absorption bandwidth since the $T_1 = 700$ ps contribution to the observed 10–20 cm^{-1} FWHM absorption bands is only about 0.01 cm^{-1}.

It is likely that the measured T_1 lifetimes represent energy relaxation within the metal–carbonyl molecules and that vibrational energy transfer to the CHCl$_3$ solvent is negligible. For the cluster compounds the CO($v = 1$) excitation probably decays into four or five quanta of ν_{MC} stretching or δ_{MCO} bending motions which is analogous to the path proposed for OH($v = 1$) relaxation. In any event, the important relaxation mechanisms clearly involve *only the vibrations* of the ground electronic state molecular system and not vibrational to electronic energy transfer. This supports the notion that cluster compounds with only a few (up to 6) central metal atoms are not large enough to exhibit free-electron or bulk metallic properties where vibrational damping by exci-

tation of the metal electrons is thought to dominate.[26–33,90,91]

Absorption and mixed bleaching-absorption transients have also been observed for the larger Rh–CO cluster compounds when the IR pulse is tuned to the peak or low frequency shoulder of the $v = 0 \rightarrow 1$ absorption. This behavior has been attributed to overtone or combination ($v = 1 \rightarrow 2$ and higher) absorptions since the anharmonic shifts of the CO stretch in metal–carbonyl systems are small (4–28 cm^{-1}). Reliable T_1 values are obtained by tuning the IR laser pulses to the high frequency absorption edge of metal–carbonyl CO-stretching features, and ensuring that the number of photons absorbed per molecule is $\leqslant 0.5$.

Extension of the current measurement technique to studies of CO chemisorbed on oxide-supported metal particles (where vibrational damping to electron–hole pair excitations may become important) is now viable. We have performed experiments for some of the same cluster compounds supported on pressed fumed silica disks (in vacuum) and find that T_1 is reduced by roughly a factor of 4 over the CHCl$_3$ data presented here. Studies of CO adsorbed on SiO$_2$ supported Pt and Rh particles have yielded $T_1 \leqslant 30$ ps for CO($v = 1$).[95,96] This reduced T_1 lifetime, when compared to those for the molecular systems studied here, is an indication that vibrational energy transfer to electronic excitation of the metal particle may indeed occur in larger metal systems.

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APPENDIX

This Appendix describes the numerical modeling of these infrared saturation experiments. A set of rate equations for the population N_i in the CO($v = i$) level of a carbonyl stretching mode:

$$dN_i/dt = R_{i,i-1}(N_{i-1} - N_i) + N_{i+1}/T_1(i+1)$$
$$- R_{i+1,i}(N_i - N_{i+1}) - N_i/T_1(i)$$

were integrated. The laser excitation rate for the $i \rightarrow i + 1$ transition is the spectral overlap

$$R_{i+1,i} = \int d\nu \sigma_{i+1,i}(\nu)I(\nu)$$

of $I(\nu)$, the pump laser intensity (photons cm^{-2} s^{-1} $\Delta\nu^{-1}$) and $\sigma_{i+1,i}(\nu)$, the absorption cross section for a transition from level i to $i + 1$. The absorption is centered at frequency $\nu_{i+1,i}$ with a Gaussian profile of width $\Delta\nu_{i+1,i}$: $\sigma_{i+1,i}(\nu) = \sigma_0 \exp[-2.77(\nu - \nu_{i+1,i})^2/\Delta\nu^2_{i+1,i}]$ and σ_0 is different for each level i. The intensity I was usually taken as a Gaussian in time (centered at $t = 0$) and frequency,

$$I = I_0 \exp(-2.77t^2/t_p^2) \exp[-2.77(\nu - \nu_L)^2/\Delta\nu^2_L]$$

with center frequency ν_L, spectral width $\Delta\nu_L$ and pulse duration t_p. In some computer runs, a sech$^2(t)$ temporal envelope was assumed. The molecular parameters of the model are the strength, central frequency, and width of the absorptions, and the level dependent $T_1(i)$ relaxation times. Al-

though the spectral parameters are well known for the CO($v = 0 \rightarrow 1$) transitions, these parameters must be estimated for $1 \rightarrow 2$, $2 \rightarrow 3$, etc. transitions. The values of I_0, t_p, v_L, and Δv_L are known. In order to simulate the experiment as accurately as possible within a rate equation model, the variation in space of the laser intensity, and hence the excited state population, was also taken into account. The spatial integration was necessary to simulate possible strong excitation (i.e., $n > 1$) at the radial ($r = 0$) center of the beam and weak excitation ($n < 1$) in the Gaussian wings. After the excited state populations (as a function of time and space) induced by the pump laser were calculated, the transmission of the weak probe pulse of intensity I_p centered at time t_d was then calculated at each point in space, from the sum of absorptions from each level

$$\sum_i A_{i+1,i}(t_d),$$

where $A_{i+1,i}(t_d)$ is the integral

$$A_{i+1,i}(t_d) = \int dt \int d\nu \sigma_{i+1,i}(\nu)$$

$$\times I_p(\nu,t,t_d)[N_i(t) - N_{i+1}(t)].$$

This is followed by a spatial integral to obtain the probe laser absorption as a function of time delay t_d. For typical values of the anharmonicity, if the laser frequency v_L is properly chosen to excite a $0 \rightarrow 1$ transition, higher $1 \rightarrow 2$, $2 \rightarrow 3$, etc. transitions overlap successively less well with the (4 cm^{-1} broad) laser pulse.

Modeling has been useful in several cases to establish conditions for which T_1 of a CO($v = 1$) level may be deduced from the semilog plots of $\ln(T/T_0)$ vs t_d. For any reasonable assumptions about the (poorly known) spectroscopy of the upper levels, computer modeling predicts that the experimental slope correctly gives T_1 providing two criteria are simultaneously met: the laser is tuned slightly higher in frequency than the $0 \rightarrow 1$ absorption maximum; and that n, the experimentally determined average number of pump laser photons absorbed per metal–carbonyl molecule, is $\leqslant 0.5$. The recommended T_1 values in Table I are from data runs meeting these criteria. As predicted, we found experimentally that when $n < 0.5$ and $v_L > v_{1,0}$, T_1 [i.e., the slope of $\ln(T/T)$ plots] was independent of the laser pulse energy and frequency, as it must be.

Modeling has also been important in deriving T_1 values which are short (i.e., comparable to the laser pulse duration). In such cases limits on T_1 may be deduced from the magnitude of the transient bleach, its width, the time t_d of peak response, and the decay time of the transient bleach compared to those parameters of the pulse autocorrelation function. We have used this deconvolution approach to derive T_1 limits for the relaxation of OH($v = 1$) vibrations of alcohols in solution,[10] and for CO($v = 1$) adsorbed on dispersed supported Pt and Rh clusters.[95,96]

The rate equation simulations have also been useful in understanding the physical basis (see Sec. IV) for the "anomolous" transient laser induced absorptions observed for the metal carbonyl molecules—but *not* observed in any of our earlier studies on the relaxation of OH or OD[10,64–66]

stretching modes for which the anharmonicities are much greater than Δv_L or $\Delta v_{1,0}$. The use of rate equations, rather than a density matrix approach, is justified for these condensed phase systems for which $T_2 \ll T_1, t_p, R^{-1}$. However, as applied to metal carbonyls, the model is significantly deficient in that it considers only population transfer within a single vibrational manifold and does not explicitly account for coupling among the various types of CO-stretching modes. Therefore, we have not used the model to derive any mode-specific kinetic parameters from the complex saturation curves (e.g., Fig. 5) which are characterized by $n > 0.5$.

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