

Four cycles of least-squares refinement yielded convergence with final agreement indexes $R_w = 0.049$ for all data and $R = 0.069$ and $R_w = 0.049$ for observed data. The final "goodness of fit" was 1.32.

A final difference Fourier contained three peaks of intensity between 0.51 and $0.73 \text{ e}/\text{\AA}^3$ which were associated with the iron atom. No other peaks of intensity greater than $0.50 \text{ e}/\text{\AA}^3$ were observed. The final atomic positional parameters and anisotropic temperature factors are listed in Table VI. Cumulant expansion coefficients for the carbonyl atoms are listed in Table VII. Lists of observed and final calculated structure factor amplitudes and the root mean square amplitudes of thermal vibration are available.²³

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Supplementary Material Available: A listing of root-mean-square amplitudes of vibrations and structure factor tables (14 pages). Ordering information is given on any current masthead page.

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Photodissociation of Molecular Beams. Cleavage of Metal-Metal Bonds in Rhenium and Manganese Decacarbonyl

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Abstract: Photodissociation of rhenium decacarbonyl has been studied in a molecular beam. The energy distribution of the photofragments obtained with incident laser light at 300 nm proves that photodissociation involves only metal-metal bond cleavage. Furthermore, two-thirds (~30 kcal/mol) of the available energy is found as internal energy (probably vibrational) of the photofragments, with the balance being translational energy. Angular distributions of the photofragments as a function of polarization of incident light were measured for both rhenium and manganese decacarbonyl. The anisotropy parameter, β , obtained from the distributions has the same value, 1.9 ± 0.3 , in both compounds; this value proves that the first strong ultraviolet absorption bands involve parallel transitions and puts upper limits of several picoseconds on the lifetimes of the excited electronic states.

Photodissociation of a molecular beam offers unique advantages in unraveling the complexities of excited electronic states. These experiments, performed in the gas phase under collision-free conditions, detail the polarization of the involved transition, set limits on the lifetime of the dissociating state, identify the photofragments, and produce information as to energy partitioning in these photofragments without the ambiguities produced by solvent interactions.¹⁻⁶ This technique has been applied to two dimetal decacarbonyls ((CO)₅M-M(CO)₅, M = Re, Mn) whose photochemistry offers unusual synthetic possibilities.⁷⁻¹¹ Both molecules have their first strong

absorption band in the near ultraviolet, the rhenium compound at $\sim 33\,000 \text{ cm}^{-1}$ and the manganese compound at $\sim 29\,000 \text{ cm}^{-1}$; these transitions are believed to involve excitation and cleavage of the M-M bond.^{10,12}

Experimental Section

The apparatus and experimental procedures have been extensively described elsewhere.^{5,6} In brief, a molecular beam is intersected at right angles by a chopped or pulsed beam of polarized light. A small fraction of molecules are photodissociated; the resulting photofragments are ionized by an electron bombardment ionizer, mass selected

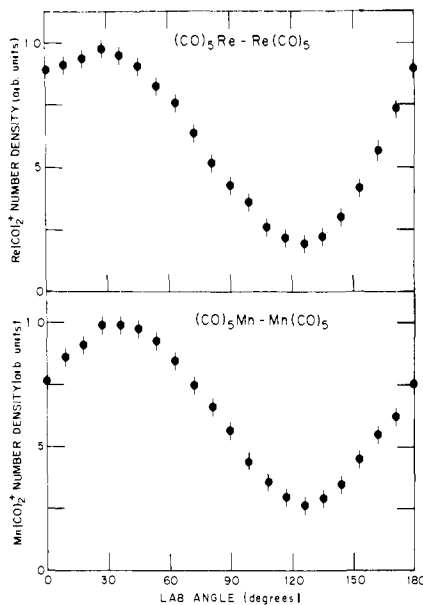


Figure 1. Photofragment angular distribution as a function of laboratory angle for $\text{Mn}_2(\text{CO})_{10}$ and $\text{Re}_2(\text{CO})_{10}$.

by a quadrupole mass filter, and detected by an electron multiplier, all of which are housed in a differentially pumped vacuum chamber along the third orthogonal axis. In the angular distribution mode, the light is produced by a kilowatt high-pressure mercury-xenon vapor lamp and chopped at 250 Hz. All wavelengths below 290 nm are removed by an inorganic filter solution¹³ (to avoid exciting higher energy absorption bands) and the resulting beam is polarized by a plastic ultraviolet polarizer. The photofragment signal is detected in the analog mode and processed by a lock-in amplifier. When a time-of-flight (TOF) spectrum is measured, pulsed ultraviolet polarized light is produced by a frequency doubled flashlamp-pumped dye laser (Chromatix CMX-4). The signal, in the digital mode, is recorded in a multichannel scaler as a function of time after the laser pulse. The energy distribution of the photofragments is derived from the TOF spectrum, the distance between the beam-light interaction zone and detector, and the masses of the photofragments. Relevant experimental parameters are given in Table I. The chemicals were bought commercially and used without further purification.¹⁴

Results

A. Angular Distributions. Photofragment intensity as a function of angle of the polarization of light has been shown to be fit by the following function:

$$I(\theta) = N \left[1 + \beta \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right) \right]$$

where N is a normalizing constant; θ is the center of mass scattering angle relative to the polarization axis; and β is an anisotropy parameter which can range from +2 for a parallel transition to -1 for a perpendicular transition. The data shown in Figure 1, when corrected for instrumental distortion and incomplete polarization of the incident light, yields a β value of 1.9 ± 0.3 for both compounds. This not only confirms the assignment of both transitions as being purely parallel,¹⁵ but also places an upper limit on the lifetime of the excited electronic state(s). If the lifetime were as long as a characteristic molecular rotation (several picoseconds for this molecule), the large anisotropy would not have been preserved.

B. Energy Distributions. The translational energy distribution of the $\text{Re}(\text{CO})_5$ photofragments is shown in Figure 2. Although the detected ion was Re^+ , the energy was calculated assuming that the parent photofragment was $\text{Re}(\text{CO})_5$; this assignment will be discussed later. On the average, only 15 kcal/mol, i.e., 33% of the available energy, is found in the translational mode. A TOF spectrum of the $\text{Mn}(\text{CO})_5$ frag-

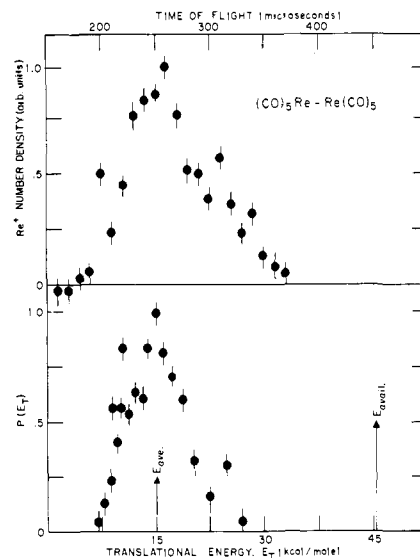


Figure 2. Time of flight (TOF) spectrum (top) and translational energy distribution (bottom) of $\text{Re}(\text{CO})_5$ fragments from photolysis at 300 nm. The flight path was 11.2 cm. A detector response time of 47 μs has already been subtracted from the data.

Table I. Experimental Parameters^a

	Re-Re	Mn-Mn
Source pressure	0.09 ^b	0.80 ^c
Beam temp	390	365
M-M bond strength ^d	51.1	22.1
Laser wavelength	300	(320)
Available energy ^e	45.7	(73.1)

^a Pressure is in Torr, temperatures in K, energies in kcal/mol, wavelength in nm. ^b A. K. Baev, V. V. Dem'yanchuk, G. Mirzoev, G. I. Novikov, and N. E. Kolobova, *Russ. J. Phys. Chem. (Engl. Transl.)*, **45**, 777 (1971). ^c F. A. Cotton and R. R. Monchamp, *J. Chem. Soc.*, 533 (1960). ^d Reference 16; recent photoelectron spectra results (M. B. Hall, *J. Am. Chem. Soc.*, **97**, 2057 (1975)) lower the first ionization potential of $\text{Re}_2(\text{CO})_{10}$ by 4.6 kcal/mol. This might raise the Re-Re bond strength by that amount. ^e $E_{\text{avail}} = \hbar\omega - D_0 + 2RT$.

ment could not be obtained because of poor signal to noise ratios. Among other problems, the product of the laser power and the molar extinction coefficient of $\text{Mn}_2(\text{CO})_{10}$, although optimized at 320 nm, was a factor of 10 lower than the corresponding product for $\text{Re}_2(\text{CO})_{10}$ at its optimum wavelength of 300 nm.

Discussion

A. Metal-Metal Cleavage in $\text{Re}_2(\text{CO})_{10}$. The TOF spectrum of Re^+ proves that the dissociation process involves only the cleavage of a metal-metal bond and not a metal-carbon bond. If one or more metal-carbon bonds were broken, conservation of momentum and energy would require the fragments to have far more than the available energy (97 kcal/mol minus bond energies). Moreover, the 95 kcal/mol photon has insufficient energy to break both the Re-Re bond (51.1 kcal/mol)¹⁶ and a Re-C bond (39.1 kcal/mol)¹⁶ and still generate an average kinetic energy of 15 kcal/mol. It should be emphasized that $\text{Mn}_2(\text{CO})_{10}$ might present a different picture. The available energy is much higher (~ 73 kcal/mol) and the metal-carbonyl bond much weaker (~ 20 kcal/mol).¹⁶

B. Energy Partitioning. A preponderance of available energy, 32 kcal/mol on the average, appears as internal energy of the two $\text{Re}(\text{CO})_5$ fragments. This internal energy could, in principle, be partitioned among the 27 vibrational and 3 ro-

tational degrees of freedom, and even the electronic energy. In fact, it will be argued, the energy appears mainly in three particular vibrational modes. First, simple pictures of the bonding in the $\text{Re}(\text{CO})_5$ radical do not predict any very low lying excited electronic states. Second, the electronic transition in the parent molecule involves the promotion of a σ bonding electron to an antibonding σ^* state;^{12,15} this is accompanied by a switching on of a repulsive potential between the Re atoms which pushes them apart but preserves the fourfold symmetry.^{17,18} Thus no torques are produced which would generate rotational energy; the internal energy will be entirely vibrational energy (or almost so). Moreover, the preservation of symmetry requires that only the six symmetric a_1 vibrations be excited.

Of these six normal modes, two correspond to very high frequency ($\sim 2000\text{ cm}^{-1}$) stretching modes of the CO ligands. These frequencies differ only slightly in different metal carbonyls and consequently they are expected to be similar in $\text{Re}_2(\text{CO})_{10}$ and in $\text{Re}(\text{CO})_5$.¹⁸ If so, the dissociation is not accompanied by any strong change in potential energy between the carbon and oxygen atoms which could excite the C–O stretch. According to our simple picture of the electronic transition, the bonding of the rhenium atom to the four equatorial CO ligands is not changed upon dissociation; however, the unpaired electron, formerly used for a Re–Re σ bond, is now in a σ antibonding state between a rhenium and an axial carbon atom. Thus a sharp change in the shape of the potential between the Re and C_{ax} atoms is expected which will excite this stretching mode. The remaining three modes are a symmetric stretch in which all four equatorial Re–C bonds stretch in phase; a symmetric equatorial carbonyl rock; and a symmetric bend in which all four equatorial COs flap up and down in phase through their original plane. The sudden motion of the Re atom, on geometric grounds, causes a larger change in the $\text{C}_{\text{eq}}\text{--Re--C}_{\text{ax}}$ and $\text{O--C}_{\text{eq}}\text{--Re}$ bond angles than in the Re--C_{eq} bond distance, thus exciting the symmetric bend and rock.

Quantum mechanically, one might describe the two excitations in the following manner. The axial stretch is a consequence of Franck–Condon factors which correlate the change in vibrational state with the change in vibrational potential. The symmetric equatorial bend and rock excitation is caused by the Re–Re repulsive potential in the excited state. The

relative magnitudes of the two excitations can be crudely estimated. The second, or dynamic, part can be roughly calculated by the impulsive spectator model¹⁹ in which the momentum of recoil is supposed to be received initially by the $\text{Re--CO}_{\text{ax}}$ group leaving the four equatorial COs as initially unaccelerated bystanders. Subsequently, the $\text{Re--CO}_{\text{ax}}$ group is slowed down by its interaction with the four equatorial COs with resulting vibrational excitation. The fraction of total energy predicted as being vibrational in this approximation is just $4M_{\text{CO}}/(M_{\text{Re}} + 5M_{\text{CO}})$ or 0.34. This would leave $\sim 1/3$ of the energy in the $\text{Re--CO}_{\text{ax}}$ stretch modes and $1/3$ in translation. The discussion above is pertinent to the initially generated vibrational distribution and not to the succeeding phenomenon of intramolecular vibrational relaxation.

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