

PRODUCTION OF EXCITED METAL ATOMS BY UV MULTIPHOTON DISSOCIATION OF METAL ALKYL AND METAL CARBONYL COMPOUNDS

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A general method is presented for the production of excited metal atoms by the photodissociation of metal alkyl and metal carbonyl compounds using the ArF or KrF laser. The process occurs collisionlessly by the sequential absorption of UV photons. Only specific fine structure components (J levels) are populated initially.

1. Introduction

One method for the production of electronically excited atoms is the photolysis of a volatile metal compound, yielding the excited metal atom as a photofragment. While there is an extensive literature on the production of excited state atoms from the photodissociation of diatomic molecules [1], the examples of excited atom production from the photolysis of triatomic and larger molecules is less common. We report here a general method for producing excited metal atoms by irradiating the vapors of various metal alkyls and carbonyls with the output of an ArF (1930 Å) or KrF (2490 Å) laser. This technique has been used to form highly excited metal atoms of iron, lead, zinc, and manganese following dissociation of different organometallic compounds in which a central metal atom is surrounded by a closed shell of ligands.

In all cases we find that the excited state atom production (1) involves the absorption of more than one photon, (2) proceeds in the absence of collisions, and (3) populates only certain specific excited state levels. The addition of buffer gas causes an enhancement in the emission intensity as well as the appearance of new lines. This method of producing excited metal atoms may provide a means of achieving laser action[†]. It may also offer the opportunity of learning

[†] Using a KrF pump laser, an iron pentacarbonyl photodissociation laser has been reported by Trainor and Mani [2]. They propose that an excited molecular species is responsible for the laser action.

how such metal-encapsulated compounds photodecompose in the intense radiation field of a rare gas halide laser.

2. Experimental

The experimental setup was straightforward. A one liter glass bulb equipped with quartz windows was filled with about 5 mtorr of a volatile metal compound. In some cases 300 torr of He or Ar was added as a buffer gas. The sample was irradiated with a focused beam of a home-built KrF laser (30 mJ, 20 ns) or ArF laser (5 mJ, 20 ns) operated at a 2 Hz repetition rate. The emission from the excited metal atoms was viewed perpendicular to the laser beam by a 1 m monochromator (SPEX 1704) having a photomultiplier with an S-20 response. A boxcar integrator (PAR model 164) provided signal averaging.

Laser photolysis of the following volatile metal compounds was studied: Fe(CO)₅ and Mn₂(CO)₁₀ from Pfaltz and Bauer; 1,1'-dimethylferrocene (DMF), butadiene iron tricarbonyl (BIT), and Mn(CO)₅Br from Strem; Pb(CH₃)₄ from ROC-RIC; and Zn(CH₃)₂ from Ventron Corp. Alpha products. All compounds were vacuum distilled before use.

3. Results

Because we had available three different iron compounds, the emission following the photolysis of

Table 1
Observed atomic iron transitions when 0.05 torr of $\text{Fe}(\text{CO})_5$, butadiene iron tricarbonyl, or 1,1'-dimethylferrocene is irradiated by the 2490 Å line of a KrF laser

Wavelength (Å)	Assignment	
	lower level	upper level
3091	$d^6s^2 a^5D_2$	$d^7p y^5D_1^0$
3527		
3308		
3526	$d^6s^2 a^5D_2$	$d^6spz^5P_3^0$
3565	$d^7s a^5F_3$	$d^7p z^3G_4^0$
3581	$d^7s a^5F_5$	$d^7p z^5G_6^0$
3619	$d^7s a^5F_2$	$d^7p z^5G_3^0$
3648 ^{a)}	$d^7s a^5F_4$	$d^7p z^5G_5^0$
3743	$d^7s a^5F_2$	$d^7p y^5F_1^0$
3816	$d^7s a^3F_4$	$d^7p y^3D_3^0$
3820	$d^7s a^5F_5$	$d^7p y^5D_3^0$
3850	$d^7s a^5F_1$	$d^7p y^5D_0^0$
3851	$d^7s a^5F_2$	$d^6spz^3P_0^0$
3896 ^{b)}	$d^6s^2 a^5D_1$	$d^6spz^5D_0^0$
3906	$d^6s^2 a^5D_1$	$d^6spz^5D_1^0$
3930	$d^6s^2 a^5D_2$	$d^6spz^5D_3^0$
3969		
4005	$d^7s a^5F_3$	$d^7p y^3F_0^0$
4046	$d^7s a^3F_4$	$d^7p y^3F_4^0$
4144	$d^7s a^3F_3$	$d^7p y^3F_4^0$
4202	$d^7s a^3F_4$	$d^7p z^3G_4^0$
4272	$d^7s a^3F_4$	$d^7p z^3G_5^0$
4308 ^{c)}	$d^7s a^3F_3$	$d^7p z^3G_4^0$
4326 ^{c)}	$d^7s a^3F_2$	$d^7p z^3G_0^0$
4384	$d^7s a^3F_4$	$d^7p z^5G_5^0$
4408 ^{c)}	$d^7s a^5P_2$	$d^6spx^5D_1^0$
4458 ^{a)}	$d^6spz^3D_3^0$	$d^7d f^3D_3$
4494 ^{a)}	$d^7s a^5P_2$	$d^6spx^5D_3^0$
4529 ^{a)}	$d^7s a^5P_3$	$d^6spx^5D_4^0$
4896 ^{b)}	$d^6spz^3D_3$	$d^6ss e^3D_2$
4925 ^{b)}	$d^6s^2 a^3P_2$	$d^7p y^3D_2^0$
4957 ^{b)}	$d^6spz^7F_4^0$	$d^6ss e^7D_4$
4998 ^{b)}		
5072 ^{a)}	$d^7s a^5F_2$	$d^7p y^5F_2^0$
5143 ^{b)}	$d^7s a^5F_3$	$d^6spz^5F_4^0$
5165 ^{b)}	$d^7p y^5F_4^0$	$d^7d g^5F_4$
5196 ^{a)}	$d^6o y^5F_3^0$	$d^7d f^5P_2$
5230 ^{b)}		
5270 ^{b)}	$d^7s a^3F_2$	$d^6spz^3D_1^0$
5411 ^{b)}	$d^7s a^5F_2$	$d^6spz^5P_3^0$
5616		
6065	broad	
6130		
6190		

- a) Seen only in DMF. b) Seen only in BIT and DMF.
c) Seen in BIT and DMF. In $\text{Fe}(\text{CO})_5$ only with added buffer gas.

$\text{Fe}(\text{CO})_5$, DMF, and BIT were studied most carefully. All three parent compounds absorb the KrF laser. Numerous atomic transitions of neutral but not ionized iron were observed, and they are collected in table 1. If there were molecular emission present, it was very weak. The most intense atomic emission in each case was the 3850 Å line ($a^5F_1-y^5D_0^0$) and the 3815 Å line ($a^3F_4-y^3D_3^0$ and/or $a^5F_5-y^5D_4^0$). The intensity of the 3815 Å line was found to depend quadratically on the KrF laser power.

Inspection of table 1 shows that in most cases only a few *J* levels (fine structure components) are populated for a given term value (see fig. 1). All transitions are from triplet and quintet states; no transitions are observed that terminate on the ground state. As the number of ligands decreases, more lines appear and the energy of the highest level populated increases: the $y^3D_3^0$ (38178 cm^{-1}) for $\text{Fe}(\text{CO})_5$; the

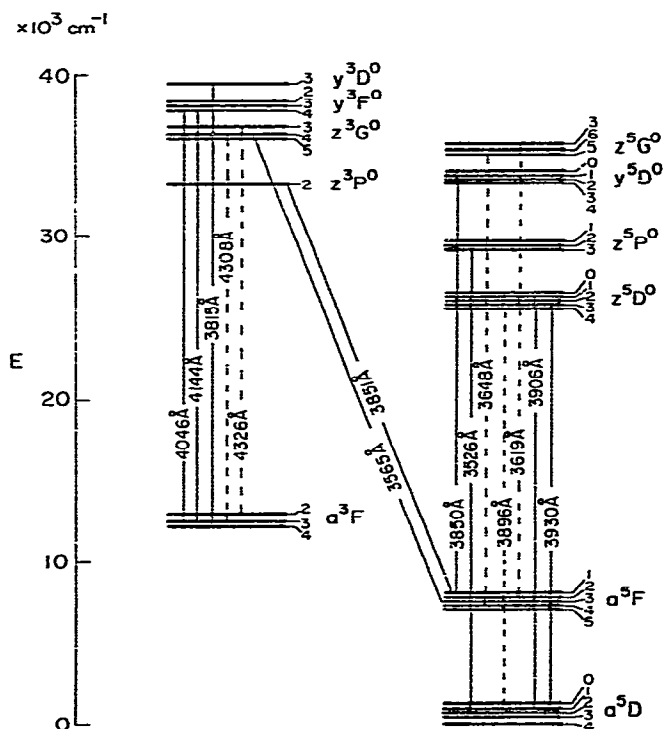


Fig. 1. The most intense atomic transitions of FeI observed in the photodissociation of $\text{Fe}(\text{CO})_5$ using the KrF laser. The dashed lines appear in addition to the solid lines when 300 torr of Ar or He is added. Table 1 contains a complete listing of the observed atomic transitions.

e^3D_2 (51740 cm^{-1}) for BIT; and the f^3D_3 (53747 cm^{-1}) for DMF.

Addition of 300 torr of Ar or He increases the intensity of the atomic transitions and causes neighboring J levels to be populated. This last fact leads to the appearance of additional atomic lines located to the blue of the low pressure lines (see fig. 1). No basic change in the emission spectrum was observed when the KrF laser was replaced by an ArF laser.

Initially, we considered the possibility that the atomic iron emission is due to direct excitation of iron atoms by the KrF laser. Trainor and Mani [2] reported that the KrF laser pumped the $^5D-^5F^0$ transition, causing strong emission between 3000 and 3040 Å. However, we must reject this possibility as the source of our atomic emission because we do not observe emission from the $^5F^0$ term value.

Both $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$ absorb the 1930 Å line of the ArF laser to yield atomic emission between 3500–5500 Å (see table 2). All lines appear sharp and are thought to be atomic manganese transitions, and most could be identified. The atomic emission from $Mn_2(CO)_{10}$ is much weaker than from $Mn(CO)_5Br$, but the same lines are observed. The strongest transition is the Mn $a^6S_{5/2}-3^6P_{3/2}$ 4031 Å line, which terminates on the ground state.

Table 3 presents the sharp lines observed between 3340 Å and 4900 Å when $Zn(CH_3)_2$ is irradiated by the KrF laser. Many transitions are not identified. No

Table 2

Observed atomic manganese transitions when 0.05 torr of $Mn(CO)_5Br$ or $Mn_2(CO)_{10}$ is irradiated by 1930 Å line of ArF laser

Wavelength (Å)	Assignments	
	lower level	upper level
3570		
3578	$d^6_s a^6D_{9/2}$	$d^6_p x^6P_{7/2}$
3807	$d^6_s a^6D_{9/2}$	$d^6_p z^6F_{11/2}^0$
3823	$d^6_s a^6D_{7/2}$	$d^6_p z^6F_{9/2}^0$
3824	$d^6_s a^6D_{5/2}$	$d^6_p z^6F_{5/2}^0$
3834	$d^6_s a^6D_{5/2}$	$d^6_p z^6F_{7/2}^0$
4031	$d^5_s^2 a^6S_{5/2}$	$d^4_sp z^6P_{7/2}^0$
4033	$d^5_s^2 a^6S_{5/2}$	$d^4_sp z^6P_{5/2}^0$
4034	$d^5_s^2 a^6S_{5/2}$	$d^4_sp z^6P_{3/2}$
5000		
5395	$d^5_s^2 a^6S_{5/2}$	$d^5_s z^8P_{7/2}^0$
5432	$d^5_s^2 a^6S_{5/2}$	$d^5_s z^8P_{5/2}^0$

Table 3

Observed emission when 0.05 torr of $Zn(CH_3)_2$ is irradiated by 2490 Å line of a KrF laser

Wavelength (Å)	Assignments	
	lower level	upper level
3346	$sp 4^3P_3^0$	$sd 4^3D_2$
3345	$sp 4^3P_2^0$	$sd 4^3D_3$
3575		
3743		
3932		
4044		
4113	$sp 4^1P_1^0$	$sd 6^1D_2$
4236		
4293	$sp 4^1P_1^0$	$ss 5^1S_0$
4298	$sp 4^1P_1^0$	$ss 7^1S_0$
4518		
4591		
4722	$sp 4^3P_1^0$	$ss 5^3S_1$
4810	$sp 4^3P_2^0$	$ss 5^3S_1$

Table 4

Observed emission when 0.05 torr of $Pb(C_2H_5)_4$ is irradiated by 1930 Å line of an ArF laser

Wavelength (Å)	Assignments	
	lower level	upper level
3220		
3640	$6p^2 \ ^3P_1$	$7s \ ^3P_1^0$
3684	$6p^2 \ ^3P_1$	$7s \ ^3P_0^0$
3800		
4023		
4030		
4058	$6p^2 \ ^3P_2$	$7s \ ^3P_1^0$
4760		
4795		
4830		
4995		
5080		
5335		
5400		
5440		
6015		
6050		

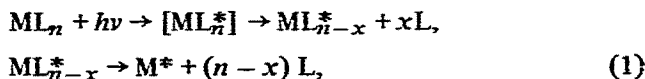
transitions are found to terminate on the Zn ground state. Both singlet and triplet states are populated.

The compound $Pb(C_2H_5)_4$ was photolyzed by the ArF laser and once again atomic emission from excited Pb atoms between 3200 Å and 6000 Å was detected (table 4). In this case, only a few lines could

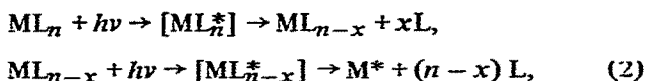
be identified. The photolysis of $\text{Zn}(\text{CH}_3)_2$ and $\text{Pb}(\text{C}_2\text{H}_5)_4$ were studied previously using spark light sources, but no atomic emission was observed [3].

4. Discussion

There are many possible models for the UV multiphoton dissociation of metal alkyls and carbonyls. Although there may be sufficient energy to cause ionization of the parent molecule, we believe that this is not the path for the production of M^* . In general, M has a lower ionization potential than that of the ligand L, and $(\text{ML}_n^+)^*$ would not be expected to fragment in a manner yielding M^* . One might picture the formation of the excited metal atom M^* from the metal-encapsulated compound ML_n as occurring through intermediate stages



or



where the ligands are denoted generically by the symbol L. Alternatively, it might be supposed that the metal-encapsulated compound, absorbs all the photons at once to form ML_n^{**} , which then throws off its ligands in one step



We believe the last mechanism does not occur. Adiabatic dissociation of ML_n^{**} should yield an excited singlet state of M^* . Even if intersystem crossing is efficient, some remnant of the singlet should manifest itself.

It is estimated that 12.2 eV of energy is required to remove all CO ligands from $\text{Fe}(\text{CO})_5$ and leave the Fe atom in the $d^8 \ ^1\text{S}_0$ state [4]. This atomic level is calculated to be located 6.6 eV above the $d^6 s^2 \ ^5\text{D}_4$ ground state. For $\text{Fe}(\text{CO})_5$ the highest lying atomic energy level of iron that is populated is several eV lower. However, there are singlet levels that are accessible and transitions from these levels are known and fall in a spectral range in which we should have ob-

served them. For example, the $d^7 p z \ ^1\text{H}_5^0$ level is located at 48382 cm^{-1} above the ground state and the $^1\text{G}_4 - z \ ^1\text{H}_5^0$ transition at 4199 \AA is reported to be strong [5]. It is also not easy to understand why only certain J levels are populated if process (3) occurs.

Processes (1) and (2) are distinguished by the time it takes an excited ML_n^* species to dissociate compared to the time it takes to absorb another photon. Since dissociation times are typically in the picosecond range [6], we suggest that process (2) best describes the photodissociation mechanism, i.e. the absorption of light causes ligands to be split out, one or a few at a time, leaving behind intermediates that can once again absorb the UV light. This model is the same as that proposed by Callear and Oldman [7,8] to explain their studies on the flash photolysis of iron and nickel carbonyls in which excited atoms were observed in absorption. This mechanism is also consistent with matrix studies in which intermediates have been trapped and identified [9]. Further supporting evidence comes from studies involving energy transfer to $\text{Fe}(\text{CO})_5$ from metastable atoms [10].

It may be likely that the last step involves the absorption of light by an ML intermediate, yielding the excited M atom:



where one or more photons are absorbed to produce M^* . In analogy to the calculations on NiCO [11], we expect that in the FeCO molecule the Fe is described by the configuration $d^7 s$ whose lowest terms are triplets and quintets. Absorption of UV light may correspond to the promotion of the $d^7 s$ orbital to a $d^7 p$ orbital. If so, this model predicts that Fe^* is primarily formed in triplet and quintet states of the $d^7 p$ configuration, in agreement with table 1. Moreover, the adiabatic dissociation of the molecular states of FeCO^* would be expected to populate only certain J levels of the Fe^* atom, again in agreement with our observations.

Much additional work needs to be done in order to refine this simple model. However, the present study demonstrates that the generation of excited metal atoms by the UV multiphoton dissociation of metal-encapsulated compounds is a general process, leading to a highly non-statistical distribution of excited atomic energy levels.

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