Iron monoxide photodissociation

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The photodissociation of ^{56}FeO was studied by means of the velocity map imaging technique. A molecular beam of iron atoms and iron monoxide molecules was created using an electrical discharge with an iron electrode in a supersonic expansion of molecular oxygen. The ground state iron atom Fe($^5D_4$) and FeO concentrations in the molecular beam have been estimated. The dissociation energy of the FeO $X\,^5\Delta$ ground electronic state was found to be D_0^0(FeO) $= 4.18 \pm 0.01$ eV. The effective absorption cross section of FeO at 252.39 nm (vac), leading to the Fe($^5D_4$)+O(^3P) dissociation channel, is $\sim 1.2 \times 10^{-18}$ cm^2. A $(1+1)$ resonantly enhanced multiphoton ionization spectrum of ^{56}FeO in the region 39 550–39 580 cm^{-1} with rotational structure has been observed, but not assigned. Angular distributions of Fe($^5D_4$) and Fe($^5D_3$) products for the channel FeO$\rightarrow$Fe($^5D_{4,3}$)+O(^3P) have been measured at several points in the 210–260 nm laser light wavelength region. The anisotropy parameter varies strongly with wavelength for both channels. © *2005 American Institute of Physics.* [DOI: 10.1063/1.1844271]

I. INTRODUCTION

The ground state of FeO has been established to be of $X\,^5\Delta_i$ symmetry with a $(4s\sigma)^1(3d\delta)^3(3d\pi)^2$ electronic configuration.[1] The manifold of electronically excited states is very complicated and less known. Recently, new bands in the region of the 16 800–18 500 cm^{-1} were discovered.[2] The first excited state, in the energy range 3948–4050 cm^{-1} is assigned as $A\,^5\Sigma^+$, and second is $B\,^5\Pi$ ($\sim 14\,400$ cm^{-1}). There are some indications of the existence of the $a\,^7\Sigma^+$ state, which is lower in energy than the $A\,^5\Sigma^+$.[3,4] Even the vibration quantum of the ground state $X\,^5\Delta_i$ is not defined: the photodetachment photoelectron spectra yield a value of 970 cm^{-1},[5,6] while optical methods suggest a value of 871 cm^{-1}.[3,7] Some low-lying potential energy curves for FeO derived from Refs. 3 and 8 are shown schematically in Fig. 1.

Studies of FeO, such as those of all transition metal oxides, have been limited by the accessibility of the species in the gas phase. Most of the early spectroscopic studies of FeO derived information on the molecular structure through a complicated analysis of spectra obtained under unfavorable conditions (high temperature ovens, discharges, laser ablation, etc.) when many rovibrational states are populated and many other species such as metal compounds or clusters are present. The cold molecular beam studies reported here have an advantage, especially when combined with velocity map imaging, which gives direct information on the molecular state (dissociation energy, possible symmetry, absorption cross section for the particular transition, etc.). In this paper we report the first direct observation of the photodissociation of FeO molecule and demonstrate two features: (1) an efficient source for metal atoms and metal compounds injected into the molecular beam, and (2) the power of the velocity mapping for analysis of poorly known molecular systems.

II. EXPERIMENT

The experimental arrangement is a typical velocity map imaging setup.[9] Briefly, it consists of a molecular beam source, lasers, ion lens system, multichannel plate (MCP) detector, charge coupled device (CCD) camera, various triggers, and supplies. In all of the laser wavelength regions one-laser experiments were carried out using tunable dye lasers (radiant dyes) pumped by the second or third harmonics of a Nd:YAG [YAG–yttrium aluminum garnet] laser. The laser light in the region 210–260 nm was obtained by doubling or tripling of the laser dyes LDS698, DCM, C500, C47) using BBO and potassium dihydrogen phosphate crystals. The ion lens system consists of the repeller, extractor,
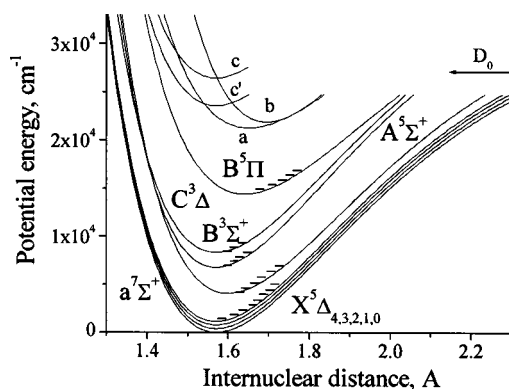

FIG. 1. Known potential energy curves for ^{56}FeO derived from Refs. 3 and 8. The $X\,^5\Delta_i$ components are strongly mixed. The arrow shows the first dissociation limit.
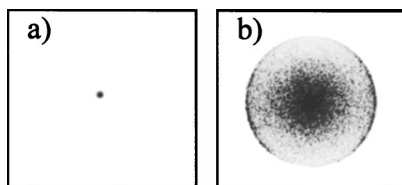
FIG. 2. Raw images observed at mass 56, with a discharge in argon (a) or oxygen (b). The laser polarization is along the vertical axis in the figure and darker areas correspond to higher signal levels. (a) probing $Fe(^5D_3)$ at 237.44 nm (vac), shows zero kinetic energy release. Using O_2 as the carrier gas, ionization at the same wavelength yields an image (b) indicating a perpendicular photodissociation producing mass 56 with product velocity 871 m/s, calibrated using $O(^3P_2)$ detection from O_2 photodissociation at 226 nm.

FIG. 3. REMPI spectrum detecting $^{56}FeO^+$ in the $39\,540–39\,580$ cm^{-1} range.

and ground electrodes, which focus ions having the same velocity to the same position on a two-dimensional (2D) MCP detector. The MCP detector converts a single ion event into a flash of light on a phosphor screen. The images observed at the phosphor screen were collected with the help of CCD camera and software (DAVIS) and averaged by a personal computer.

Special attention was directed to the design of the molecular beam source, which is capable of generation of metal atoms and their compounds formed by reaction with the carrier gas. The details of the design have been described in a recent paper.[10] It consists of a holder for a high voltage discharge wire loop installed on the top of standard pulse nozzle (general valve). The electrode from desirable material (iron in this case) can be plugged in and supplied with a dc voltage of $-1000--2000$ V. The front side of the nozzle acts as the second (grounded) electrode. When the nozzle opens and the gas pulse enters the chamber, it causes a corona discharge around the high voltage electrode. This discharge injects atoms from the electrode surface into the gas volume. The mechanism for metal atom injection is similar to the "cathode sputtering" effect, when free metal atoms appear in the discharge near the cathode. In our experiments the cathode was made from iron wire $\varnothing0.5$ mm, turned into a ring of $\varnothing3$ mm. The discharge current was limited by the high voltage supply to 10 mA.

III. RESULTS AND DISCUSSION

Typical raw images observed from a discharge in argon/oxygen at mass 56 amu, are shown in Figs. 2(a) and 2(b).

$(1+1)$ resonantly enhanced multiphoton ionization (REMPI) detection of $Fe(^5D_3)$ atoms [Fig. 2(a)] in an Ar carrier gas discharge yields a zero-velocity image as expected. When oxygen was used as the carrier gas this image changes to Fig. 2(b), showing the central dot and also a new disk with kinetic energy release. Furthermore, a signal at mass 72 amu appeared in the molecular beam after the discharge which shows zero kinetic energy and a two-photon intensity dependence. We assign this mass as ^{56}FeO. During a arbitrary scan of the $39\,500–39\,850$ cm^{-1} photon energy region a REMPI spectrum has been found (Fig. 3), which to the best of our knowledge represents the first reported

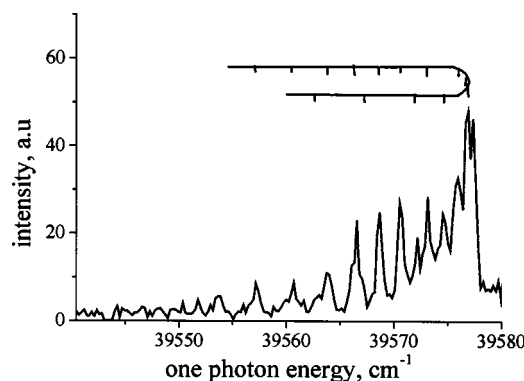REMPI spectrum for FeO. This is a relatively strong signal, comparable to the $(1+1)$ REMPI signals for Fe atoms in the beam.

Due to lack of data, we cannot assign this spectrum, but most likely it shows a rotational progression with turning point near $39\,577$ cm^{-1}. Emission from excited FeO has been reported at slightly higher energies than the observed spectrum.[7]

As indicated by the ring in Fig. 2(b), when using O_2 as the carrier gas instead of argon an iron-containing molecule is photodissociated, yielding a fragmentation channel at the mass of iron with nonzero kinetic energy release. In Fig. 4 we prove that the appearance spectrum of this ring from Fig. 2(b) coincides well with that for atomic iron (Fig. 3). The immediate conclusion is that the products of photofragmentation are neutral $Fe(^3D_J)$ atoms, not Fe^+ ions. A rough estimate of the J-state distribution of the cold $Fe(^3D_J)$ beam is ~240 K. Photodissociation of FeO around 252 nm yields qualitatively a "colder" J distribution, but we did not attempt to make these measurements quantitative. The angular distributions for the $J=4$ and $J=3$ state products at this wavelength were similar.

With velocity map imaging it is possible by measuring the kinetic energy of the products at set of wavelengths to determine: (1) The binding energy of the parent molecule. (2) The mass of the coproduct of the dissociation. A one-laser experiment has been performed through the $210–260$ nm wavelength region where there are a number of
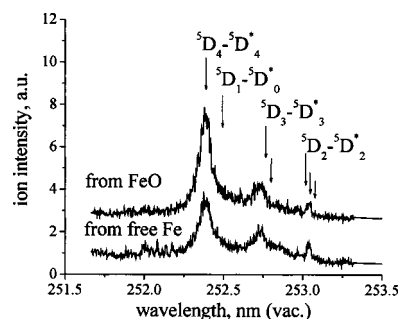

FIG. 4. Yield spectrum of Fe^+ ions with and without kinetic energy release in the $251.5–253.5$ nm region. Resonant states in the $(1+1)$ REMPI process are indicated in the figure.
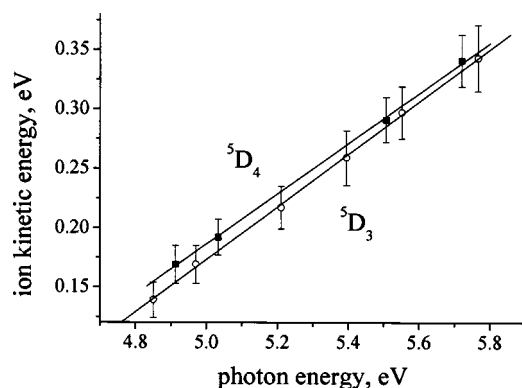
FIG. 5. Kinetic energy release of the fragment iron atoms in two different (^3D_J) states as a function of wavelength measured in the 251.5–253.5 nm region.

possibilities to detect $Fe(^5D_4)$ $Fe(^5D_3)$ products by $(1+1)$ REMPI. The results of kinetic energy measurements are shown in Fig. 5.

Both of the sets show the same linear dependence on the photon energy, and their slopes indicate that the other photodissociation product has the mass 15.9 ± 0.5 amu. This indicates that we observe the dissociation of $^{56}Fe^{16}O$. By extrapolating these sets we find the dissociation energy values of 4.18 ± 0.01 eV for the lowest dissociation channel, giving rise to $Fe(^5D_4)$ and 4.225 ± 0.01 eV for the upper one, giving rise to $Fe(^5D_3)$. We assume here that the molecules FeO in molecular beam are in the ground electronic state and vibrationally cold. This is supported by the sharp image without structure observed for Fe atoms arising from photodissociation of FeO [Fig. 2(b)]. The experimentally measured dissociation energy value for the lowest channel gives directly $D_0^0(\text{FeO}) = 4.18 \pm 0.01$ eV. The extracted dissociation energy for the upper channel involves also the energy of the excited fine state $Fe(^5D_3)$. Taking into account the energy difference between iron atom fine states $E_{Fe(^5D_3)} - E_{Fe(^5D_4)} = 415.9298$ cm^{-1}, the value for the upper channel gives $D_0^0(\text{FeO}) = 4.173 \pm 0.01$ eV which is in agreement with the value measured for lowest channel. For comparison, the literature value for $D_0^0(\text{FeO})$, 4.23 ± 0.13 eV (Ref. 8) is obtained by thermo chemical methods, the value 4.17 ± 0.08 eV given in Ref. 11 is mainly the averaged result of earlier spectroscopic studies, and 3.65 eV was obtained in the recent theoretical calculations.[12]

Examination of Fe and FeO ion signals as a function of laser fluence allows the concentrations of Fe atoms and FeO molecules to be estimated as 2×10^6 and 8×10^6 cm^{-3}, re-

spectively. An estimation of the absorption cross section of FeO molecule in the ground state gives a value of 1.2×10^{-18} cm^2 at 252 nm.

Angular distributions of the $Fe(^5D_4)$ and $Fe(^5D_3)$ products were also obtained at several dissociation wavelengths and found to fluctuate widely.

IV. CONCLUSIONS

^{56}FeO dissociation has been studied for the first time by velocity map imaging. Absolute values of the $Fe(^5D_4)$ and FeO concentrations in molecular beam have been estimated. Angular distributions of the $Fe(^5D_4)$ and $Fe(^5D_3)$ products for the channel $FeO \rightarrow Fe(^5D_{4,3}) + O(^3P)$ have been characterized for several laser wavelengths in the 210–260 nm region. The anisotropy parameters differ for the two channels and oscillate with wavelength. The dissociation energy in the ground $X\,^5\Delta$ state of FeO has been measured and found to be $D_0^0(\text{FeO}) = 4.18 \pm 0.01$ eV.

The experimental effective absorption cross section of FeO at 252.39 nm, leading to $Fe(^5D_4) + O(^3P)$ dissociation channel has been estimated as 1.2×10^{-18} cm^2. A rotational band of the $(1+1)$ REMPI spectrum of ^{56}FeO in the region 39 550–39 580 cm^{-1} has been obtained, but not assigned.

[1] A. S.-C. Cheung, R. M. Gordon, and A. J. Merer, J. Mol. Spectrosc. **87**, 289 (1981).
[2] J. Lei and P. J. Dagdigian, J. Mol. Spectrosc. **203**, 345 (2000).
[3] G. Drechsler, U. Boesl, C. Bäßmann, and E. W. Schlag, J. Chem. Phys. **107**, 2284 (1997).
[4] M. Krauss and W. J. Stevens, J. Chem. Phys. **82**, 5584 (1985).
[5] J. Fan and L.-S. Wang, J. Chem. Phys. **102**, 8714 (1995).
[6] P. C. Engelking and W. C. Lineberger, J. Chem. Phys. **66**, 5054 (1977).
[7] A. J. Merer, Annu. Rev. Phys. Chem. **40**, 407 (1989).
[8] G. Balducci, G. De Maria, M. Guido, and V. Piacente, J. Chem. Phys. **55**, 2596 (1971).
[9] A. T. J. B. Eppink and D. H. Parker, Rev. Sci. Instrum. **68**, 3477 (1997).
[10] D. A. Chestakov, A. Zawadska, D. H. Parker, K. Vidma, A. V. Baklanov, and S. A. Kochubei, Rev. Sci. Instrum. (to be published).
[11] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
[12] C. W. Bauschlicher and J. P. Maitre, Theor. Chim. Acta **90**, 189 (1995).