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Spectroscopic studies of AIO in argon matrices

S. J. Bares,^{a)} M. Haak, and J. W. Nibler

Department of Chemistry, Oregon State University, Corvallis, Oregon 97330

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The diatomic species AlO has been isolated in argon at 18 K as an Al + O_2 reaction product and shown to produce intense laser induced fluorescence in the visible. An infrared-optical double resonance experiment has established the X state vibrational fundamental at 975 cm⁻¹, one of four possibilities previously proposed from infrared studies. ¹⁸O experiments further establish the assignment. The apparent low infrared intensity of the AlO stretch is consistent with a recent *ab initio* calculation of an oscillator strength of 4×10^{-7} . This anomalously low value is confirmed by comparison of infrared and visible absorption intensities for similar samples. A v'' = 1 lifetime in excess of 6 ms was directly measured for AlO by the double resonance method. This slow rate of radiative relaxation makes AlO attractive as a probe molecule for vibrational relaxation studies.

I. INTRODUCTION

In recent years matrix isolation methods have proven quite useful in the study of energy transfer processes in simple solids. Much of this work has been motivated by an interest in the mechanisms by which a vibrationally excited molecule dissipates excess energy when surrounded by weakly interacting host atoms or molecules.¹ The use of laser excitation and fluorescence lifetime techniques (LIF) in investigating vibrational relaxation in matrices has been pioneered by Bondybey and Brus and applied extensively to the study of vibrationally excited electronic states.^{1(b)} Relaxation here is generally fast $(10^{-9}-10^{-4} \text{ s})$ and frequently involves cascading via interleaved levels from lower lying electronic states.

Less is known about relaxation in ground electronic states although some measurements have been made using double resonance²⁻⁴ and infrared fluorescence^{5,6} methods. Results to date show that this energy can degrade via local or extended lattice translational or rotational modes, via transfer to a vibrational acceptor molecule or via purely radiative processes. Lifetimes range from 10^{-9} to many seconds but the factors which determine the relaxation rates and the relative importance of the decay channels are not well understood.

More data for ground electronic states of simple model compounds are needed but these are difficult to obtain for experimental reasons. Direct IR pumping with IR fluorescence monitoring (IR-LIF) does permit single state excitation but suffers from limited laser tuning range and low detector sensitivity. An optical-optical double resonance technique (OODR) offers much greater detection capability but is less selective in the absorptionemission pumping of the ground state and the decay analysis is thereby complicated. Clearly an infrared pump, optical probe combination (IODR) would retain the advantages of both approaches and we report here the first such application for a matrix isolated molecule, the diatomic species AlO.

AlO was chosen as a promising candidate for such studies because its fundamental vibrational transition (965 cm⁻¹ in the gas phase⁷) lies near the output region of a CO₂ laser. Also, this frequency lies well above matrix lattice modes so that a relatively long lifetime might be expected. Finally, AlO has a convenient $B {}^{2}\Sigma^{+}-X {}^{2}\Sigma^{+}$ transition which yields an intense gas-phase LIF spectrum in the blue-green region.⁸ This system has been well characterized in previous matrix studies using absorption spectroscopy.⁹⁻¹¹ However, many molecules which fluoresce strongly in the gas phase, such as I₂, show only weak, broad emission in inert gas matrices and at the outset of this work it was not known whether similar quenching would occur for AlO.

For direct IR pumping, the exact frequency of the AlO infrared absorption in an argon matrix must be known. There have been several infrared studies of the aluminum oxides in matrices,⁹⁻¹² but much uncertainty remains about the species responsible for the rich spectrum in the 900–1000 cm⁻¹ region. In particular, the AlO stretching frequency in argon has been assigned various values, ranging from 917 to 975 cm⁻¹. To date, only the visible absorption bands near 450 nm can be positively correlated with AlO.

In the present work, AIO has been prepared in argon matrices and shown to produce intense and discrete LIF spectra. Infrared spectra have been obtained and a positive identification of the AIO absorption has been made by an IODR experiment. This has established the feasibility of this method for vibrational relaxation studies and these will be reported in a subsequent publication. As an important adjunct to this energy transfer work, the spectroscopic results reported here give an estimate of AIO concentration and provide some information about the

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^{a)} Current address: Exxon Research and Engineering, Clinton Township Rt 22E, Annadale, New Jersey 08801.

identification and relative concentration of other products formed in the generation of AlO.

II. EXPERIMENTAL

Matrices were prepared by continuous codeposition of Ar/O_2 mixtures (4–16 mmol/h) and Al atoms on a polished aluminum substrate cooled to 18 K by a Displex closed cycle helium refrigerator. Ar (Matheson UHP 99.9995%) and O_2 (Airco 99.5%) samples were prepared on a greaseless vacuum system evacuated to 0.1 mTorr or better. Oxygen concentrations of 1% were used in most experiments and pressures were measured with a calibrated Pirani gauge (Granville Phillips 275) and a 1000 Torr pressure transducer (Validyne AP10-42). Oxygen 18 (Stohler Inc. 95%) samples were prepared in the same manner for several experiments.

Some difficulty was encountered in finding a reproducible source of Al atoms since liquid Al, as well as its vapor, is extremely caustic to most materials used for Knudsen cells. Graphite is porous to liquid Al and Ta and Mb both form amalgams with it. This problem was solved by using boron nitride (Carborundum Co., HP, low O_2) as a crucible to contain the aluminum. This white, chalky material was not chemically attacked at the highest temperature used (1600 K) and could be easily machined for insertion into a 3/8" by 1 3/8" Ta heating jacket. The latter was resistively heated and was configured so that the limiting orifice for evaporation was a 1 mm hole in the boron nitride. Evaporation temperatures of 1400 to 1500 K were used and were monitored with an optical pyrometer.

The reaction of Al and O_2 is known to occur in the gas phase with zero activation energy and AlO is a significant product of this reaction.⁸ In these matrix experiments this vapor phase reaction occurred quite readily, as indicated by a faint blue chemiluminescence just above the matrix surface. In some experiments, subsequent photolysis of the matrix was carried out at 121.6 or 253.7 nm, but this had little effect on the features attributed to AlO.

Infrared spectra were recorded in a reflection mode¹³ using a Perkin–Elmer 180 spectrometer at a resolution of about 1 cm^{-1} and with a frequency uncertainty of about 0.5 cm^{-1} . Optical absorption spectra were obtained using a sapphire substrate and a Cary 15 spectrophotometer. The range from 250 to 700 nm was covered and the measured absorption wavelengths have an uncertainty of about 1 nm. Fluorescence spectra were excited by a Spectra-Physics argon ion laser with 50–100 mW slightly focused at the sample frozen on the aluminum substrate. The emission was collected and dispersed by a Spex 1402 double monochromator equipped with a cooled RCA 31034 photomultiplier tube. The uncertainty in the wavelengths of the emission features is estimated at about 0.2 nm.

For the IODR experiment, an Apollo XAT CO_2 laser was employed as a pump source. This pulsed laser was obtained as government surplus and was originally designed for resistor trimming. It was modified for tuna-

bility by addition of a 75 line/mm grating blazed at 10 μ in first order. The micrometer of the grating rotation mount was calibrated by measuring the laser wavelength with the infrared spectrometer. Output was obtained only on the stronger CO₂ lines, with pulses of 20 W peak power and a near Gaussian time profile with FWHM of 125 µs. An Eltec pyroelectric detector was used to monitor the infrared beam. The optical fluorescence was generated using a Chromatix CMX-4 dye laser with a pulse duration of about 1 μ s. The infrared and visible beams were overlapped at the sample and Coumarin 480 dye (Exciton) was used to generate blue output to match the AlO 1''-0'absorption. The emission was monitored by the Spex instrument, set to the 0'-0" fluorescence maximum. For improved S/N, the photomultiplier signal was ratioed against the dye laser output by a PDP 11/10 computer which was also used for timing and signal averaging purposes. A schematic of the experimental apparatus is shown in Fig. 1.

III. RESULTS AND DISCUSSION

A. Optical absorption spectra

Figure 2 shows a matrix absorption spectrum of the reaction products formed by codepositing Al with an Ar/ O₂ = 100 mixture at 18 K. Of central importance are the relatively broad bands at 456.9 and 439.7 nm. These are blue shifted with respect to the gas phase transitions of AlO at 484.6 0"-0' and 465.1 nm 0"-1' but the spacing between the matrix features (~860 cm⁻¹) matches that in the gas (865 cm⁻¹). Support for the 456.9 nm assignment as the band origin comes from the good agreement of the intensities with the indicated Franck-Condon values calculated using the anharmonic oscillator method of Bates.¹⁴ These same matrix absorptions have been seen by others⁹⁻¹¹ using a variety of methods of generating AlO and the spectral assignment seems certain.

Other features in the absorption spectrum can also be identified. Abe and Kolb¹⁵ have studied Al/Ar matrices and the absorptions we observe at 338 and 289 nm are in good agreement with bands they assign to electronic transitions of Al atoms. From concentration variations, they have shown that the broad feature we see near 399 nm is due to Al₂ dimer. The source of the weak band near 417 nm is not established but, in view of the high O₂ concentration in our samples, may be Al₂ perturbed by a nearby O₂ molecule. The complete absorption below 240 nm is attributed to O₂ and also to Al₂O. The latter is known to absorb near 210 and 265 nm^{10,15} and is certainly expected to be present in our samples.

To obtain reasonable absorbances of the AlO bands, a relatively high Al concentration and a thick matrix were needed. For the experiment corresponding to Fig. 2, the Knudsen oven was operated at 1500 K and the deposition period was 90 min. A crude estimate of the initial Al/Ar ratio can be deduced from vapor pressure data and the effusion relations of Miller.¹⁶ Assuming uniform mixing and complete condensation on the 1" sapphire substrate, a maximum Al concentration of 1%

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FIG. 1. Schematic diagram of the infraredoptical double resonance apparatus. PD = photodiode, PY = pyroelectric detector.

is calculated for a film of 0.4 mm thickness. Most of the Al will be consumed in the gas phase by reaction with O_2 and it is interesting to compare this maximum with



FIG. 2. Visible–UV absorption spectrum of Al + O₂ reaction products isolated in Ar at 18 K. Sample formed by 90 min deposit of 1% O₂/Ar mixture with Al beam generated at a Knudsen cell temperature ($T_{\rm Kn}$) of 1500 K, followed by 30 min photolysis at 253.7 nm. Indicated below the lower trace are the relative Franck–Condon intensities calculated for AlO.

the Al concentration estimated for the matrix using the absorbance at 338 nm. For this calculation we use the gas phase oscillator strength, as modified by Finn *et al.*¹⁰ for an argon matrix (0.107), and obtain a value of 3 ppm. Although both calculations are probably good only to an order of magnitude, they do indicate nearly complete reaction of the Al and that the resultant products are well isolated.

Further evidence that most of the Al was consumed in the initial formation of the matrix comes from the fact that no major intensity changes of the Al and AlO bands were observed when oxygen atoms were produced by *in situ* 121.6 nm photolysis. Only the features at 399 and 417 nm showed any photosensitivity, decreasing threefold in intensity for the sample of Fig. 2 after the sample had been exposed to 30 min of 253.7 nm light from a high pressure mercury lamp. This may be due to reaction of Al₂ with O₂ to form Al₂O₂, a product known to exist from mass spectroscopic and infrared matrix studies.

B. Fluorescence spectra

As indicated in Fig. 2, the 456.9 nm 0"-0' transition of AlO is nearly coincident with the 457.9 nm argon ion laser line and, indeed, strong fluorescence was seen when matrix samples were irradiated at this wavelength (Fig. 3). Similar spectra were produced by excitation at 454.5 and 465.8 nm but the fluorescence was less intense since these exciting lines fall in the shoulders of the 0''-0'absorption. Although all the emission bands are broad, from the spacings in Fig. 3 and in other spectra, we obtain a rough value of 974 \pm 10 cm⁻¹ for the ground state vibrational fundamental in an argon matrix. This is close to the gas phase value of 965 cm^{-1} for AlO. Moreover the relative Franck-Condon intensities of the matrix bands are in good accord with those calculated using the gas phase molecular parameters of AlO [Fig. 3(c)].

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FIG. 3. Fluorescence spectra of AlO excited by several argon ion laser lines. Sample is isolated in Ar at 18 K and was prepared as in Fig. 1 caption except $T_{\rm Kn} = 1400$ K. At the bottom are shown calculated relative Franck-Condon intensities.

It is interesting that the 0''-0' emission bands do not appear at the same wavelength when different excitation lines are used. This could arise if phonon relaxation in the upper state is not complete on the nanosecond time scale of emission. Alternatively, one may have a distribution of AlO in different matrix orientations or sites so that the change in excitation wavelength would produce emission from AlO subgroups in different environments. Some annealing and concentration studies were undertaken to test these possibilities but the results were not illuminating. A tenfold decrease in O₂ concentration merely reduced the fluorescence intensity by a factor of about 2. Comparable intensity changes resulted when the Al concentration was increased or decreased by a factor of 5 relative to the conditions corresponding to Fig. 3. Only when the Al concentration was increased more than tenfold (Knudsen temperatures > 1550 K) did the band shapes change appreciably, with a weak broad shoulder appearing 6 nm to the red of each fluorescence feature. These bands are attributed to AlO perturbed by a nearby Al atom.

At high Al concentrations, fluorescence was also seen from 560 to 650 nm. This consisted of a sequence of 18 broad lines spaced by about 210 cm⁻¹ and was independent of excitation wavelength over the range 457.9-514.5 nm. The dimer species Al₂ seems a likely candidate for this red emission since its A-X transition has been observed at 580.2 nm in the gas phase.^{7,15} However, the observed spacing does not match the Al₂ ground state spacing of 350 cm⁻¹. The extra structure could be due to interleaved emission sequences from different upper state levels or from dimers in more than one site. It is also possible that the fluorescence originates from higher aggregates of Al which are so far uncharacterized.

C. Infrared spectra

The fluorescence spectra yield a rough value of 974 \pm 10 cm⁻¹ for the ground state vibrational fundamental of AlO in an argon matrix. This range offers the chance of laser excitation by one of the CO₂ R branch transitions which have a spacing of 1.3 cm⁻¹. To more precisely define the AlO frequency and to further characterize the Al + O₂ reaction products, infrared spectra were recorded for matrix samples.

Figure 4 shows the spectrum obtained in the region of interest for a sample prepared under conditions similar to those for the visible absorption experiment of Fig. 2. At these high Al concentrations, features are apparent at 993, 975, 965, 944, 912, and 886 cm⁻¹; at lower Al levels, only the 993 and 912 cm⁻¹ bands were detected. Most of these transitions have been seen in previous studies⁹⁻¹² and all workers agree on the assignment of the strongest feature at 993 cm⁻¹ as the antisymmetric stretch of Al₂O.

The assignment of the other bands is unsettled. In an early study, Linevsky *et al.*¹² studied products formed by evaporation of $Al_2O_3 + Al$ mixtures and commented that "the possibility that weak features near 978 cm⁻¹ may arise from AlO cannot be excluded." Knight and Weltner⁹ observed two strong bands at 993 and 917 cm⁻¹ in argon matrices of products formed from Al_2O_3 in W or W/Rh cells heated to 2500 K. Since mass spectral measurements indicate that AlO and Al_2O are the dominant vapor species at this temperature, the 917 cm⁻¹ band was assigned as AlO. Two weaker features at 975 and 944 cm⁻¹ were detected but were not assigned. Finn *et al.*¹⁰ used a hollow cathode device to sputter Al atoms for reaction with Ar/O_2 flows prior to matrix deposition. They did not see the 917 cm⁻¹ band for matrices which



FIG. 4. Infrared spectrum of Al + O_2 reaction products isolated in Ar at 18 K. Sample was prepared as in Fig. 1 caption except $T_{Ka} = 1450$ K. Lower portion of the figure shows the visible fluorescence intensity as the CO₂ pump laser was tuned from line to line while keeping the visible probe laser fixed at the 1"-O' absorption wavelength.

gave intense AIO absorption in the visible region. Instead they assigned a feature at 946.5 cm⁻¹ to AlO and reported an ¹⁸O counterpart shifted 45.5 cm⁻¹ to lower frequency. It should be noted that this shift does not agree well with the predicted harmonic value of 33.6 cm⁻¹. Their spectra also show two weak features between 960 and 980 cm⁻¹ which they do not discuss. Yarkov et al.¹¹ studied the formation of AlO from Al + N_2O reactions and attribute a matrix band at 965 cm^{-1} to AlO.

D. Infrared-optical double resonance experiment

The IODR experiment proved useful in selecting among the alternative assignments of the AlO fundamental. The CO₂ pump laser was tuned from line to line while monitoring the visible fluorescence produced by the visible probe laser tuned to excite only the v'' = 1 state. As shown in Fig. 4, no fluorescence was detected as the CO_2 laser was tuned across the 944 cm⁻¹ region and hence this absorption must be attributed to some other aluminum oxide such as Al₂O₃, Al₂O₂, etc. However a pronounced maximum was observed at the R(18) line at 974.9 cm⁻¹, firmly establishing 975 cm⁻¹ as the AlO stretching fundamental. The double resonance signal was quite strong and disappeared if either laser source was blocked. It also decreased as the visible probe laser was delayed with respect to the pump pulse and a v'' = 1lifetime of ~ 6 ms was determined for the sample conditions of Fig. 4. Under more dilute conditions this lifetime was increased.

The 975 cm⁻¹ value for AIO is consistent with the range of 974 \pm 10 cm⁻¹ deduced above from our visible fluorescence measurements. This range would also permit a possible assignment of the weaker 965 cm^{-1} feature as AlO but this could not be tested by the double resonance method since no CO₂ laser output was obtained over this band. The 975/965 intensity ratio varied from experiment to experiment and in some cases no 965 cm⁻¹ absorption was seen. It seems likely that this feature could be AlO perturbed by a nearby O_2 or N_2 molecule. N_2 would have been a likely matrix neighbor in the Al + $N_2O \rightarrow AlO$ + N_2 reaction of Yarkov et al.¹¹ and this interpretation could account for their assignment of the 965 cm⁻¹ feature to AlO.

Several ${}^{18}O_2$ doping experiments were carried out and a double resonance maximum similar to that of Fig. 4 was observed for Al¹⁸O at the P(22) line at 942.4 cm⁻¹. Considering the coarse line spacing of the CO₂ laser, this shift of 32.5 cm^{-1} is in excellent accord with the harmonic value of 34.6 cm⁻¹. Both maxima were seen in mixed isotopic samples when the visible probe laser was set for the Al¹⁶O resonance, a result not inconsistent with the broad absorption width of the electronic transition (Fig. 2).

It is interesting that the vibrational frequency of AlO shifts slightly (1%) to higher frequency in going from gas to argon matrix. This is the opposite direction of most "ionic molecules" such as the alkali halides whose frequencies decrease 3%-10% due to the dielectric effect of the solvent. Several authors^{9,17} have discussed the bonding in AlO and suggest that the $X^{2}\Sigma^{+}$ ground state acquires ionic character by mixing with the $B^{2}\Sigma^{+}$ state (the lowest state to dissociate to ions $Al^+ + O^-$). Since the gas phase X-B separation is observed to *increase* (5%) in argon, this mixing would be expected to be smaller in the matrix and the ground state to be less ionic, as observed.

E. Concentration of AIO

In all of the infrared experiments, AlO was expected to be a major product and it is surprising that the stretching absorption should have such low intensity. A likely explanation is suggested by the recent ab initio calculations of the dipole moment function for the Xground state of AlO by Lengsfield and Liu.¹⁸ These results indicate that this function is relatively constant during vibration, due to a gradual transition from Al^+O^- to $Al^{++}O^{-}$ as the bond length decreases. The authors calculate a vibrational band oscillator strength of $(4 \pm 3) \times 10^{-7}$, an extremely small value which may account for the difficulty in identifying this absorption in the matrix studies.

Using this f value and our measured absorbance of the 975 $\rm cm^{-1}$ feature, an AlO matrix concentration of about 20 ppm is deduced. This can be compared with a value of 2 ppm calculated from the visible absorption spectrum of Fig. 2 using the B-X(0'-0'') oscillator strength of 0.027 measured for the gas phase.⁸ Given the uncertainties in such estimates, the agreement is satisfactory and these results establish that the AlO concentration was a few ppm in these matrices. For the double resonance experiments, strong signals were observed even when the Al flux was reduced by a factor of 30 and hence even greater dilution of all reaction products can be assumed.

IV. SUMMARY

Infrared and electronic spectra have been obtained of the matrix isolated products of the $Al + O_2$ reaction and the identities and rough concentrations of a number of species have been determined. Laser excitation of the B-X transition of AlO produces strong visible fluorescence. An infrared-optical double resonance experiment has established the AlO vibrational frequency as 975 cm^{-1} in argon matrices and has demonstrated the potential of this system for energy transfer studies. The low oscillator strength of this transition implies a radiative lifetime of 4 s for the v'' = 1 vibrational state. This estimate may be shortened by a factor of 2 due to the dielectric effect of the argon matrix but even then the value is abnormally long. This slow rate of radiative decay makes AlO especially attractive as a candidate for examining nonradiative relaxation mechanisms involving the host and various dopants of known concentration. Detailed studies¹⁹ show that direct V-V transfer plays a dominant role in the energy dissipation process and this work will be described in a subsequent publication.

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