Cavity-Ringdown Spectroscopy Studies of the B^2Σ^+ ← X^2Σ^+ System of AlO

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Aluminum is the second most abundant metal in the Earth’s crust and, in view of its appreciable cosmic abundance, it is also of interest in astrophysics.[1] The metal is frequently used as a rocket fuel and, as a result of both military launches and the space program, considerable amounts of aluminum oxide are annually introduced into the atmosphere, which makes its chemistry and effect upon atmospheric processes topics of considerable interest.

Both the diatomic AlO[2±5] and the triatomic Al_2O_3[6] oxides were previously studied by optical spectroscopy. The best known transition of the simplest oxide (AlO) is the B^2Σ^- ← X^2Σ^- system, with an origin near 20688 cm\(^{-1}\), which has been investigated extensively both through theory[7] and experiment.[8] In the laboratory, the oxides have been prepared by a number of techniques, but mostly in various discharges or flames.[9] It has also been detected in the upper atmosphere after the release of organoaluminum compounds.[10±12] Two higher-lying states of AlO, denoted C^2Π and D^2Σ^+, are known. Several years ago Towle et al. employed laser-induced fluorescence to examine the C^2Π ← X^2Σ^- transition[13] in some detail. The lowest excited state, A^2Π, has only been observed in absorption in low-temperature matrices by Knight and Weltner.[14]

In the most extensive study of the B^2Σ^- ← X^2Σ^- system, Coxon and Naxakis produced the oxide by discharge through a flowing mixture of aluminum chloride and oxygen, and analyzed some 25 bands ranging up to v’ = 9 and v’’ = 6.[15] By fitting their data, they obtained the molecular constants of AlO for both states involved. They could also resolve the spin-rotation doubling of P-branch lines of some of the bands. Resolution was possible, depending on the signal-to-noise ratio for a given band, only for the higher P-branch lines above a certain minimum value ranging from J = 15 – 28. They found that the spin-doubling constants in the two Σ states are strongly correlated, so that only the difference γ’ – γ” could be determined. Based on their data they concluded that for the B state, γ’ exhibits only small linear variation with v’, whereas in the ground state it changes rapidly from v’ = 0 to 6. The doubling in the ground state is undoubtedly due to interactions with the lowest A^2Π state, which is known from the matrix data of Knight and Weltner to lie near 5400 cm\(^{-1}\), in the neighborhood of the v’ = 6 ground state level.[13]

One of the difficulties of discharge or furnace studies is spectral congestion, and the commiserate extensive line overlapping in the high-temperature spectra. Vibrational constants in the X and B states are very similar, so that individual sequence bands are very closely spaced and overlap. Furthermore, the R branches form heads near J = 15, so that the spin-rotation doubling could not be resolved, and in many cases it was even impossible to assign any R-branch lines.

A typical survey spectrum in the region near the origin of the B^2Σ^- ← X^2Σ^- transition showing the Δν = 0, 1, and 2 sequences is presented in Figure 1. Even though we do not use a slit valve, strong absorptions of diatomic AlO are clearly observable. The aluminum oxide in our system is undoubtedly formed by the gas-phase reaction of aluminum atoms with molecular oxygen. The product is formed hot, and our spectrum shows clearly that even though many collisions take place between AlO formation and the spectral measurement, ground-state levels up to at least v’ = 2 are significantly populated. While the distribution is not strictly thermal, using Franck-Condon factors for the B-X transition the intensities can be fairly well approximated by an AlO vibrational temperature around 1500 K.

For six vibronic bands of this system we have recorded a higher-resolution, rotationally resolved spectra. Examination of relative intensities indicates, as often is the case, a nonthermal distribution. A logarithm plot of the 0–0 band intensities in Figure 2 shows the non-Boltzmann multitemperature rotational distribution.

More specifically, since J’ = 7 – 8 are the levels with the highest population, one can deduce that T < 100 K, and the same value is obtained by a least-squares fit of the J = 1–16 levels. This confirms that some 80% of the molecules have been cooled by the supersonic expansion to less than one-third of the ambient temperature. On the other hand, a separate fit of the very weak lines corresponding to levels with J ≈ 25 yields a temperature of more than 1100 K, suggesting that some 5% of the molecules exhibit a temperature close to the ≈ 1500 K value deduced from the vibrational level populations. Experiments carried out with slightly changed expansion conditions or laser alignment indicate that this effect cannot be fully explained by a nonuniform temperature in the expanding jet. At least partially, this seems to reflect a dependence of rotational-level collisional relaxation on J, with the closely-spaced low levels relaxing very efficiently. The process becomes less efficient for levels above J = 25, where their spacing becomes larger than the collisional (kT) energies. A number of years ago, a much more extreme

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example of this effect was observed during a study of \(^{3}\Sigma_{u}^{+}\) \(^{3}\text{He}_{2}\) molecules in a flowing afterglow at liquid nitrogen temperatures: Under these circumstances, a distribution of low rotational levels, described very well by \(T \approx 80\) K, was followed by a clear gap and then very high rotational levels appeared, described by a truncated \(\approx 3000\) K distribution.\(^{14}\) Apparently in our experiments, the molecules are initially formed with vibrational and rotational temperatures of around 1500 K. Most of the molecules are then very efficiently rotationally cooled in the supersonic expansion, but there is little vibrational cooling. Also, a small fraction of the molecules in very high rotational levels retain the signature of the initial temperature at which they were formed.

A distinct advantage of measuring the spectra in supersonic expansion is the lower translational temperature, resulting in sharper lines, as well as the lower rotational temperature. Under these conditions there is much less overlap in the individual sequence bands than in a flowing gas, and in addition there are few high-\(J\) lines of other bands to obscure the band origin one wishes to analyze. One can clearly see in Figure 3 that, unlike the high-temperature spectra, the band origin and both the \(P\)- and \(R\)-branches are clearly visible and...
rotational distribution with temperatures $T_\text{rot}$ observable down to $J$. To improve the low resolution, the spin-rotation doubling is

![Figure 3. Logarithm of the scaled intensities of the 0–0 band rotational lines, $\nu(2J) + 1$, versus $J(2J + 1)$. The plot shows the non-Boltzmann, multitemperature rotational distribution with temperatures $T_\text{rot} \approx 105$ and 1100 K.](image)

recognizable, and low lines down to $R = 0$ and $P = 1$ are easily identified and assigned. Even without the use of an etalon to improve the low resolution, the spin-rotation doubling is observable down to $J \approx 10$ and is fully resolved for $J > 20$.

It should be noted that the temperature of about 100 K, which characterizes the molecular translations in our experiment, and the rotational intensities in the spectrum presented in Figure 1 are determined by the experimental conditions of the supersonic expansion. To study the spectroscopy of light diatomic molecules, very low temperatures are not needed and are actually undesirable. In experiments of this type, with rotational temperatures of below 10 K, only the very lowest $J$ levels are populated, resulting in little information about the rotational structure and very inaccurate rotational constants. In many such cases in fact, we had to try to modify the experimental conditions in order to “heat” the product molecules. If needed for larger or heavier species, the temperatures in our experiments can easily be further lowered by changing the expansion conditions and increasing the stagnation pressure, in particular if a larger vacuum pump were substituted for the existing one. Actually, the fact that in our source we use a conventional nozzle with a circular aperture should allow us to reach lower rotational temperatures than the specially designed slit valves often used in cavity-ringdown experiments.

**Experimental Section**

We constructed an apparatus which combines a laser vaporization supersonic expansion source with the very sensitive detection technique of cavity-ringdown laser absorption spectroscopy.\(^{15-17}\) A pulsed piezoelectric valve of our own design was used in the source. The jet with the absorbing species to be investigated was located inside a high-finesse optical cavity consisting of two highly reflecting mirrors. A fraction of the tunable probe laser pulse entered the cavity upon each reflection through the highly reflecting mirrors. By fitting the decreasing intensity of the transmitted signal, one obtains the “cavity-ringdown” time. In the absence of a sample, this time depends mainly on the reflectivity of the mirrors. When the laser was tuned to a frequency where the molecular species in the jet absorb, the cavity losses increased and resulted in a shortened ringdown time.

The laser vaporization source, which was previously described,\(^{14, 16}\) operated at the second harmonic of a Nd-YAG laser. The Al source was a vaporized aluminum disk, with helium being used as the carrier gas. Even without any addition of oxygen, the oxide bands could easily be detected. A time-of-flight mass spectrometer (TOF-MS) attached to the source chamber permitted the detection and identification of the species produced in the vaporization source, which also allowed conditions for producing the desired molecule, AlO in this case, by adding controlled amounts of oxygen to the carrier gas to be optimized.

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