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Vibrational Relaxation and Electronic Quenching-Rate Coefficients for BiF ($A0^+$, v^1) by SF_6

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We have extended our kinetic data base for the A-state of BiF to include SF_6 as a collision partner. By applying a four-level finite-difference fitting routine to time-resolved fluorescence traces from v' = 0-3, we have obtained rate coefficients for electronic quenching, as well as for vibrational relaxation within the A-state manifold. As was the case for our previous results with He and Ar, electronic quenching is slow in comparison to radiative decay. Vibrational relaxation does not show a simple v' dependence, but rather, for the levels examined, increases markedly for higher v'. Our results confirm the suitability of SF_6 as a bulk diluent in the proposed NF/BiF chemical laser system.

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VIBRATIONAL RELAXATION AND ELECTRONIC QUENCHING-RATE COEFFICIENTS FOR BiF ($A0^+$, v') BY SF_6

Renewed interest in bismuth monofluouride (BiF) has been created by the observation of its blue A → X emission in flow-tube experiments concerning energy transfer between NF(a^1D) and Bi(^4S). This result generated interest in the potential for BiF(A) to act as the lasing species in a chemically driven electronic-transfer laser based on the efficient H + NF_2 → NF(a) + HF reaction. More recently, the rate coefficients for spontaneous emission, electronic quenching, and vibrational relaxation (V-T) for the A-state have been measured[2] in Ar and He by means of laser-induced fluorescence (LIF) of BiF generated in a Broida oven.[3] Similar measurements were also made in the presence of SF_6, but the resulting data were not reproducible. It was thought that the unreliable nature of that experiment was due to the catalytic decomposition of SF_6 on the hot surfaces of the oven as a result of the method used to introduce the quenching gas. This assumption was born out by the presence of elemental sulfur on the walls of the cell. The experimental apparatus has been modified to isolate the gas-mixing region from the hot oven containment region. The modified design has enabled us to obtain consistent and reproducible results. We report here the rate coefficients for the electronic quenching and vibrational relaxation of BiF (A, v' = 0,1,2,3) by SF_6 at ≈450 K.

Details of the experimental arrangement have appeared previously.[2] The Broida oven/LIF cell has been modified so that the metal-vapor generator is physically isolated from the mixing and observation region of the cell by a stainless-steel bulkhead. Figure 1 is a schematic diagram of the apparatus. An alumina crucible containing Bi metal is supported by a W coil that is resistively heated to ≈1000 K. A flow of Ar is used to sweep the metal vapor from above the hot crucible. A dilute concentration of F_2 (10% in He) is introduced by means of an annular injector into the entrained Bi flow, which exits the oven section through a stainless-steel

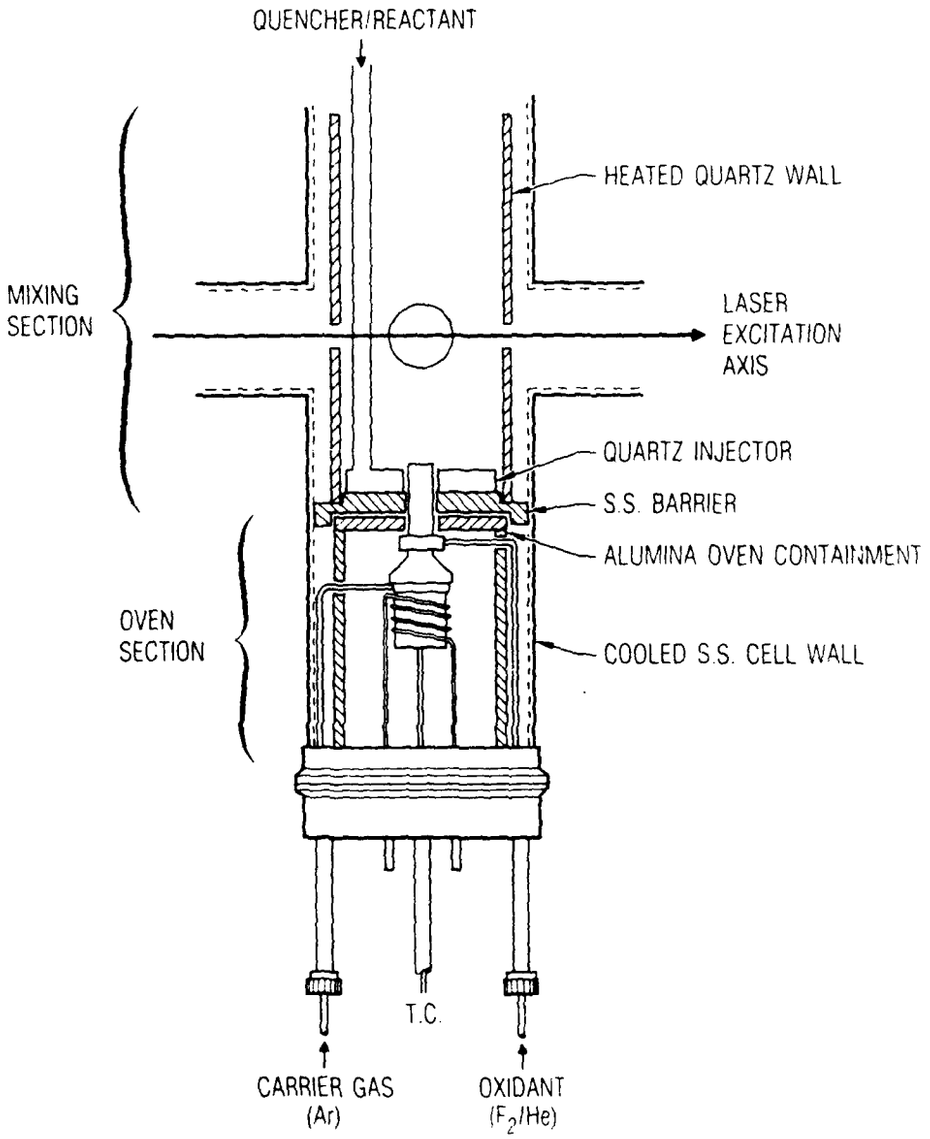

Fig. 1. Diagram of the Modified Broida Oven/LIF Cell

stack extending 2 cm beyond the bulkhead. The quenching gases are introduced immediately above the bulkhead by means of a quartz-ring injector. Gas flow rates are measured by mass flow meters. The cell pressure is monitored by a capacitance manometer. The entire mixing region is enclosed in a quartz shroud that has ports to pass the laser beam and to allow observation of the LIF. The shroud can be resistively heated to maintain temperatures in the flow of up to 200°C. Temperatures are determined by thermocouples.

An excimer-pumped dye laser tuned to the bandhead of the (1,0) transition at 429.6 nm is used to create the initial BiF(A, v' = 1) population. This population is then redistributed among adjacent vibrational levels of the A-state manifold by collisions with SF_6. The time-resolved fluorescence from v' = 0, 1, 2, and 3 is collected through appropriate narrowband filters (1 nm FWHM) by a photomultiplier and is recorded via a 100-MHz transient digitizer.

In order for the time dependence of the system to be extracted, the data from each vibrational level for a given set of experimental conditions must be proportional to the relative population of that level. This is accomplished by scaling each fluorescence trace according to (1) the fractional transmission of each band through its corresponding filter, (2) the Franck-Condon factor for the transition, and (3) the responsivity of the photomultiplier as a function of wavelength and cathode voltage. The resulting internally consistent data set is then fit by a four-level, finite-difference routine that requires best guesses of the rate coefficients as input. The coefficient of the reverse vibrational-relaxation rate is calculated by detailed balance; the fitting routine is performed iteratively until a single set of coefficients, capable of fitting data taken under a variety of experimental conditions, is obtained. Figures 2(a) and (b) show data taken at two different total pressures and SF_6/Ar ratios, as well as the corresponding data fits.

Our results are given in Table 1. Previously obtained rate coefficients for He and Ar are included for comparison. The error inherent

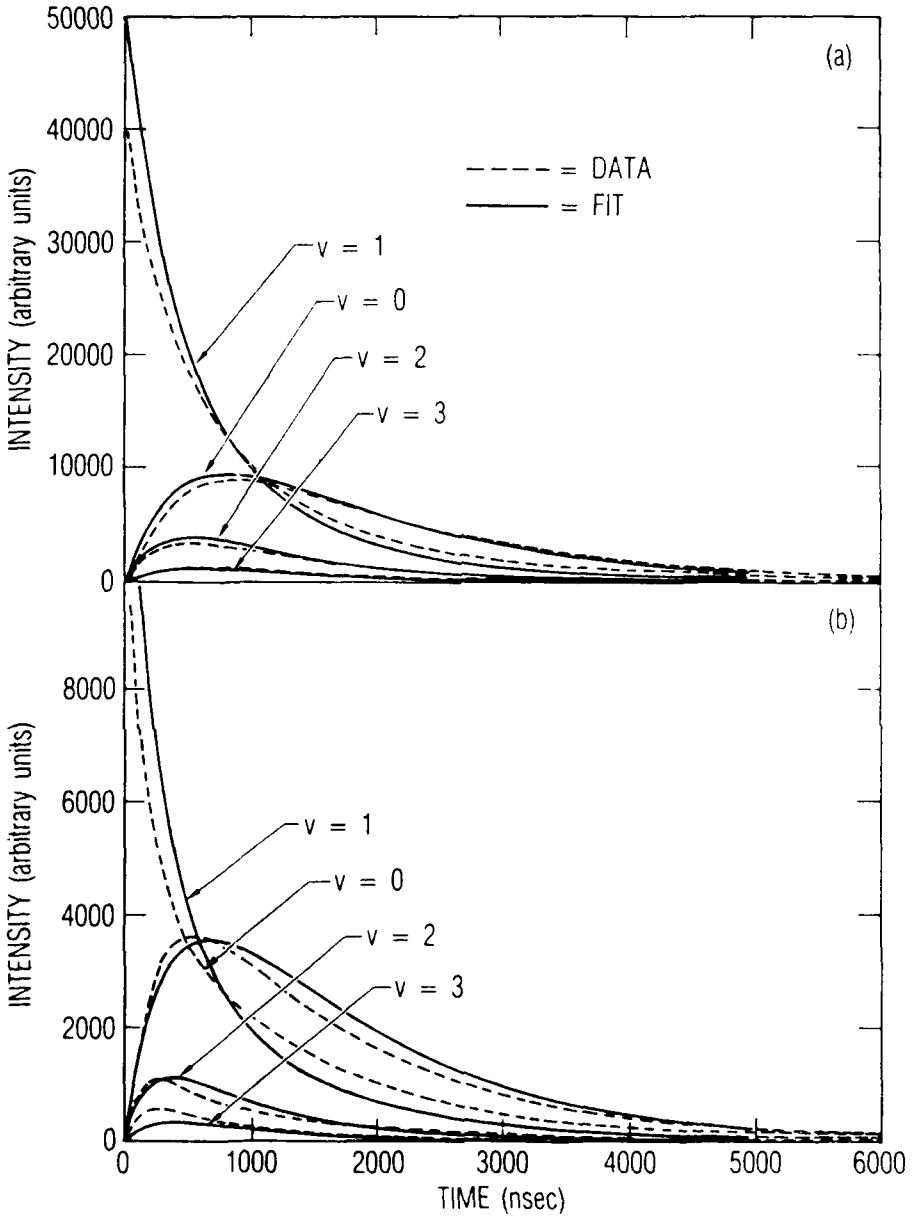

Fig. 2. Fluorescence Time Histories from BiF (A, v = 0,1,2,3) and Their Corresponding Fits at (a) a Total Pressure of 9.69 Torr and a SF_6/Ar Ratio of 1.2 and (b) 12.0 Torr and a SF_6/Ar Ratio of 5.4

Table 1. Vibrational Relaxation and Electronic Quenching-Rate Coefficients for BiF ($A0^+$) in SF_6. The rate constants for He and Ar were determined previously[2] and are listed here for comparison.

Level	BiF (A,v → v-1), cm^3/molec-sec			BiF (A,v → X), cm^3/molec-sec		
	SF_6	Ar	He	SF_6	Ar	He
v = 0				9.5×10^{-14}	3.8×10^{-13}	3.5×10^{-13}
v = 1	5.2×10^{-12}	1.5×10^{-12}	6.1×10^{-12}	1.1×10^{-13}	4.3×10^{-13}	3.8×10^{-13}
v = 2	1.1×10^{-11}	5.7×10^{-12}	1.8×10^{-11}	1.3×10^{-13}	5.0×10^{-13}	4.3×10^{-13}
v = 3	2.6×10^{-10}	1.1×10^{-11}	3.5×10^{-11}	1.5×10^{-13}	8.1×10^{-13}	5.0×10^{-13}

in our method of obtaining the rate constants is most apparent in the discrepancy between the data and the fit for v' = 1. To test the data and our method of normalizing them to relative intensities, we summed the scaled data from all four levels of a set. The resulting trace was fit to a single exponential that decayed according to the radiative lifetime of BiF(A), indicating the consistency of the data and our normalizing procedure. On the basis of the variation between the best fits for individual data sets, we estimate our experimental error to be about ~50%.

In our previous experiments we reported V-T rate coefficients for He and Ar that scaled as $v^{1.7}$ for v' = 1-3. The rate coefficients for vibrational relaxation with SF_6 do not demonstrate a simple v' dependence, as they scale approximately as v' for $k_{1\rightarrow 0}$ and $k_{2\rightarrow 1}$ but increase by over a factor of 20 for $k_{3\rightarrow 2}$. This dramatic increase in the efficiency of vibrational transfer may reflect an increased contribution of V-V processes to the overall thermalization of the A-state vibrational manifold. The vibrational energy separation of BiF(A) approaches resonance with the ν_6 mode of SF_6 for higher v' ($\Delta E_{v3,2}$ = 363 cm^{-1} vs. 344 cm^{-1} for ν_6). It should also be noted that the coefficients quoted for electronic quenching represent upper limits of the actual values. At the pressures obtainable in this experiment, radiative decay is the dominant removal process for the A-state. As a result, the model used to fit the data was insensitive to coefficients smaller than those stated.

The influence of SF_6 on BiF A-state kinetics is of interest because of its impact on issues concerning scaling to an actual laser device based on the $H_2 + NF_2$ chain reaction.[4] Of particular importance to the NF^*/BiF system is the ability to moderate the reaction thermally. This is necessary in order that gas mixtures of sufficiently high reactant densities may be used without deflagration following photoinitiation. With its large number of internal states and correspondingly high heat capacity, SF_6 is an ideal bath gas. The results reported here indicate that it also efficiently relaxes the higher vibrational levels while also being, in relation to its radiative lifetime, a slow electronic quencher of BiF(A).

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