

Laser-Induced Fluorescence: A Method to Measure the Internal State Distribution of Reaction Products*

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Reactive scattering studies have been greatly stimulated by the advent of the "supermachine," a molecular beam apparatus that includes universal detection by electron-impact ionization and mass analysis of the ions.¹ However, this device does not seem well-suited for determining the vibrational-rotational (v'' , J'') distribution of the reaction products. We report here molecular beam experiments using laser-induced fluorescence as a means of product detection. This method seems capable of providing detailed information about

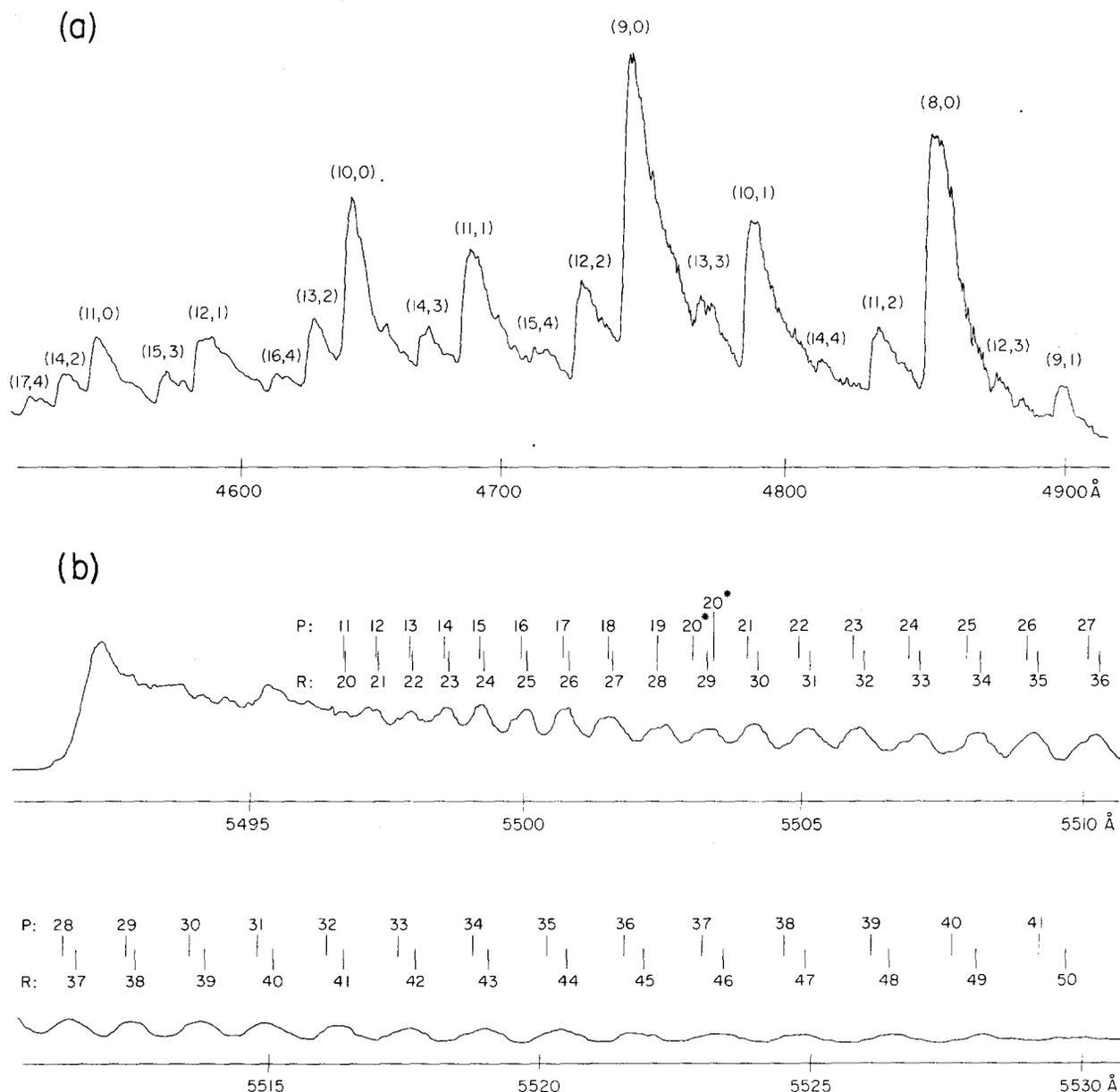


FIG. 1. The BaO fluorescence signal as a function of laser wavelength: (a) fast scan showing vibrational distribution; (b) slow scan showing rotational distribution of the (3, 0) band. The asterisks mark a perturbation.

the population of the final quantum states for a wide class of reactions.

In a molecular beam apparatus,² a thermal beam of barium atoms ($T \approx 1100^\circ\text{K}$) intersects an uncollimated, thermal beam of O_2 molecules ($T \approx 300^\circ\text{K}$) and reacts to form $\text{BaO}(X^1\Sigma) + \text{O}(^3P) + 0.66 \text{ eV}$. Simultaneously, light from a pulsed (2–10 nsec duration), tunable dye laser³ passes through the reaction zone. As the wavelength of the dye laser is scanned, the BaO molecules are excited to the (v', J') level whenever the laser wavelength coincides with an allowed $v''J'' \rightarrow v'J'$ transition in the A–X band system. The resulting fluorescence emitted at right angles to the laser beam is detected by a fast-response photomultiplier. The laser pulse triggers a boxcar integrator (Princeton Applied Research or Keithley Instruments) whose electronic gate (window) is maintained open from the time of the laser pulse to 2–5 times the BaO A state lifetime. This analog device permits us to average the signals resulting from many laser pulses. The scattered light from the laser beam is rejected either with a sharp cutoff Corning filter or by delaying by typically 20 nsec the opening of the electronic gate.

The BaO fluorescence rate versus laser wavelength is shown in Fig. 1. Figure 1(a) gives the vibrational structure in a fast scan; Fig. 1(b) shows the partially resolved rotational structure in a slow scan. In the latter, the assignments are according to Lagerqvist *et al.*⁴ Other measurements were taken between 5200–6500 Å.

The BaO fluorescence rate is proportional to the ground state population $N_{v'',J''}$, the Franck–Condon factor⁵ $q_{v',v''}$, and the laser intensity $\rho_{v'',v''}$ at the wavelength of the $v''J'' \rightarrow v'J'$ transition. The ground state vibrational distribution $N_{v''}$ may be obtained simply from the data shown in Fig. 1(a) by comparing the band intensities $I^{v''v''}$ with the *same* v' but *different* v'' , since the ratio $I^{v''v_2}/I^{v''v_1}$ is equal to

$$N_{v_2} q_{v',v_2} \rho_{v',v_2} / N_{v_1} q_{v',v_1} \rho_{v',v_1}$$

Alternatively, if band intensities of different v' levels are compared, the spectral response of the detection system must be known. Preliminary analysis of the data yields the population ratios $N_0:N_1:N_2:N_3:N_4:N_5:N_6:N_7 = 1.00:0.53:0.37:0.30:0.20:0.13:0.11:0.10$, which fits moderately well a Boltzmann distribution of 2500°K . The average vibrational energy is approximately 0.25 eV, about one-third of the total energy available (reaction exothermicity plus initial kinetic energies of the reactants).

The rotational distribution may be obtained from data such as that shown in Fig. 1(b). In order to

achieve the resolution shown, it is necessary to use about 5 times higher O_2 densities than necessary for the vibrational population measurements. Thus, although a Boltzmann distribution of about 500°K fits well the present data, this must be considered a lower limit because of collision-induced rotational relaxation. However, the relative vibration population we have obtained is not expected to be significantly relaxed.

We are also able to measure directly the BaO A state radiative lifetime. Using a swept narrow sampling window, our first lifetime measurements for $v' \geq 3$ give a value of $350 \pm 50 \text{ nsec}$, in reasonable agreement with Johnson.⁶

Recently, other groups have also investigated the $\text{Ba} + \text{O}_2$ reaction using molecular beam techniques. Fricke, Kim, and Fite⁷ suggest that the total reaction cross section is about 1 \AA^2 . Batalli-Cosmovici and Michel⁸ have obtained the differential cross section for relative collision energies between 0.3–1.0 eV. They report evidence for rebound-type scattering from which they conclude that not only the chemical energy released but also a good deal of the initial translational energy is found in product excitation. However, Loesch and Herschbach⁹ have remeasured the differential cross section at similar relative collision energies (0.3–0.7 eV), and they find instead evidence for the formation of a collision complex. Our measurements at relative collision energies of about 0.1 eV are consistent with the existence of a collision complex and show that less than half the total energy available goes into vibrational excitation of the products.

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¹ J. L. Kinsey, "Molecular Beam Reactions," Biennial Review of Science, Technology, and Medicine, Reaction Kinetics (to be published).

² Similar to that in C. D. Jonah, R. N. Zare, and Ch. Ottinger, *J. Chem. Phys.* **55**, 263 (1972).

³ Dial-A-Line AVCO laser modified by us to give a 0.5 Å bandwidth.

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⁵ Calculated using the programs in R. N. Zare, UCRL Report, UCRL-10925, 1963.

⁶ S. E. Johnson, *J. Chem. Phys.* **55**, 149 (1972).

⁷ J. Fricke, B. Kim, and W. L. Fite, *Proceedings of the VII ICPEAC, Abstract of Papers* (North-Holland, Amsterdam, 1971), p. 37.

⁸ C. Batalli-Cosmovici and K. W. Michel, *Chem. Phys. Letters* **11**, 245 (1971).

⁹ H. J. Loesch and D. R. Herschbach (private communication).