

IMPROVED DETERMINATION OF OVERALL ROTATIONAL AND VIBRONIC RELAXATION RATES OF $\text{BaO}(A^1\Sigma, v' = 8, J' = 49)$ COLLIDING WITH Ar

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Using the linear dependence of the ratio of direct and indirect integrated rotational line fluorescence on the inverse Ar pressure, we obtain more accurate rate constants for rotational relaxation: $k = (91.3 \pm 1.9) \times 10^3 \text{ Pa}^{-1} \text{ s}^{-1}$ and for vibrational plus electronic relaxation: $k = (21.0 \pm 0.9) \times 10^3 \text{ Pa}^{-1} \text{ s}^{-1}$ of cw-laser-excited $\text{BaO}(A^1\Sigma, v' = 8, J' = 49)$ in collision with Ar. The experiments were performed on BaO produced in a gas-flow system using oxidants N_2O , O_2 and CO_2 at variable argon pressures.

1. Introduction

In laser-induced fluorescence (LIF) experiments, excitation of one specific rovibronic level can be obtained due to the small linewidth of the laser light. Both time-dependent [1,2] and steady-state [3–10] applications of this method have been used in the study of excited-state collisional relaxation of homonuclear [3–7] as well as of heteronuclear [1,2,7–10] diatomic molecules, with different perturber gases (mostly rare gases).

After excitation of a specific rovibronic level, other levels will also be populated due to inelastic collisions. The fluorescence intensity from each level is a probe for the probability of a collisional transition to that level. Under single-collision conditions, i.e. if the radiative lifetime of the excited state is short compared to the inverse collision frequency, these intensities will increase linearly with perturber gas density. At higher densities deviations from this linear dependence will be found as an increasing number of excited molecules undergo more than one collision before they radiate. In many of the experiments it was uncertain that single-collision conditions were met. In this paper we de-

rive an exact relation between perturber gas density and the ratio of *direct* and *indirect* fluorescence intensity; this ratio is related immediately to the ratio of the numbers of excited molecules radiating without or with previous inelastic collision(s). We use this relation to determine overall rate constants for rotational relaxation and for vibrational relaxation together with quenching of $\text{BaO}(A^1\Sigma, v' = 8, J' = 49)$ in Ar. The relation we derive holds also under *multiple* collision conditions.

The precision obtained with this new method can be demonstrated by a comparison with previous measurements made by Gottscho et al. using optical-optical double resonance [11,12]. From measured state-to-state rate constants, they have calculated overall cross sections for rotational relaxation of $\text{BaO}(A^1\Sigma, v' = 1, J' = 0 \text{ or } 15)$ in Ar. Johnson [10] has measured quenching rate constants of $\text{BaO}(A^1\Sigma)$ in He for various initial vibrational levels: we cannot, however, compare his results with ours as we have not separated vibrational relaxation from quenching in the experiments reported here. In a forthcoming paper we shall report on this separation that is now in progress.

A preliminary version of our present paper has been presented [13].

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2. Theory

An excited BaO molecule can decay through four different channels:

- (1) radiative decay before the molecule has undergone any inelastic collision;
- (2) radiative decay after the molecule has undergone rotation-changing collisions only;
- (3) radiative decay after the molecule has undergone vibration- and (possibly) rotation-changing collisions, but no quenching collisions; and
- (4) quenching (electronically inelastic collision).

In the first case we speak of *direct line fluorescence*, in the second of *indirect line fluorescence*, in analogy to atomic fluorescence [14]. Together they are called *direct band fluorescence*. By contrast the fluorescence which occurs in case (3) is called *indirect band fluorescence*. No fluorescence at all will be seen in case (4).

At a given perturber gas pressure p the probabilities for the different kinds of inelastic collisions per unit of time can be written as follows, using the bimolecular rate constants k_j :

- (1) $k_r p$ for a rotation-changing collision;
- (2) $k_v p$ for a vibration-changing collision, and
- (3) $k_q p$ for a quenching collision.

The probability of a radiative transition per unit time is given by the Einstein coefficients A and does not depend on the initial rotational quantum number. The fraction of laser-excited molecules that exhibit direct line fluorescence is then given by

$$A/[A + (k_r + k_v + k_q)p] . \quad (1)$$

Similarly, the fraction of molecules showing direct band fluorescence is

$$A/[A + (k_v + k_q)p] . \quad (2)$$

By subtracting the direct line fluorescence intensity from the direct band fluorescence intensity, one finds an expression for the indirect line intensity integrated over all rotational levels. The intensity ratio of direct and indirect line fluorescence is

$$\frac{I_{\text{dir}}}{I_{\text{ind}}} = \frac{A}{k_r} \left(\frac{1}{p} + \frac{k_v + k_q}{A} \right) . \quad (3)$$

By plotting $I_{\text{dir}}/I_{\text{ind}}$ versus $1/p$ one finds values for the overall rotational relaxation rate constant and for the sum of the rate constants for quenching and vibrational relaxation. Analogously, one can separate the

latter two rate constants by plotting the intensity ratio between direct and indirect band fluorescence versus $1/p$.

From eq. (3) we note that for $p \rightarrow \infty$, $I_{\text{dir}}/I_{\text{ind}}$ remains finite, so direct line fluorescence will always be distinct as a peak in the spectrum. It should be noted that all intensities need only be measured *relative* to the direct line intensity.

3. Experimental

We excited BaO molecules to the $A^1\Sigma, v' = 8, J' = 49$ state by using a cw Ar⁺ laser with an output power of ≈ 4 W at 488 nm (Coherent CR 10). BaO is produced by melting Ba metal in a Broida-type oven (e.g. refs. [10,15,16]), consisting of an alumina crucible heated by a tungsten filament. An argon gas flow carries vapourized Ba into a reaction chamber where it meets an oxidant (N_2O , CO_2 , O_2).

The apparatus allows us to vary the partial pressure of each of the components independently as well as the total pressure for a fixed gas composition. A high-resolution monochromator (Jobin-Yvon H.R. 1000) with a maximum attainable resolution of 0.01 nm was used to analyze the fluorescence spectrally. For the experiments reported here, however, we needed only a resolution of ≈ 0.1 nm. A second monochromator with much lower resolution (≈ 100 nm) was used to monitor the total fluorescence. It was permanently tuned to the complete BaO $8 \rightarrow 1$ fluorescence band.

Data acquisition was performed by an on-line Apple microcomputer that also controlled the monochromator. This computer instantaneously divided the spectral intensity by the monitor signal. In this way variations both in laser intensity and frequency and in Ba vapour production were compensated for. The microcomputer also performed the required spectral integrations.

Pressure is measured by a capacitance manometer (Baratron) with a range of 100 Torr. Readings give true absolute pressure, independent of gas composition.

4. Results

In the experiments reported here we scanned the

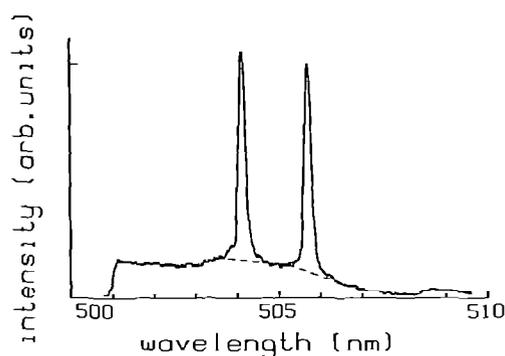


Fig. 1. $\text{BaO}(A^1\Sigma, v' = 8 \rightarrow X^1\Sigma, v' = 1)$ fluorescence band after excitation of $J' = 49$. Total argon plus oxidant (5%, N_2O) pressure was 137.5 Pa. The dashed lines show how direct line fluorescence was separated from indirect line fluorescence.

full $8 \rightarrow 1$ band of the $\text{BaO}(A^1\Sigma \rightarrow X^1\Sigma)$ transition without resolving the rotational structure. Direct line fluorescence manifests itself as two peaks – corresponding to the P and R lines – superimposed on a smooth background spectrum of smeared out indirect line fluorescence (see fig. 1). We took scans at various pressures with constant percentage, as well as with two different constant partial pressures, of oxidants O_2 , N_2O or CO_2 .

In separating direct from indirect line fluorescence intensity we assumed that the background varied smoothly under the two direct line peaks. We interpo-

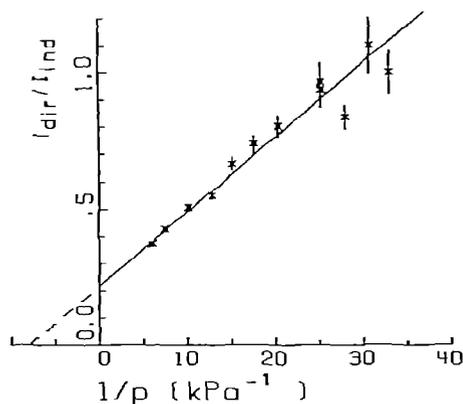


Fig. 2. Ratio of direct and integrated indirect line fluorescence intensities as a function of the inverse argon pressure. 0.4 Pa of CO_2 served as an oxidant for these measurements. The intercept of the straight line with the horizontal axis is a direct measure of $k_v + k_q$ (see eq. (3))

lated it by drawing a straight line and integrated the intensity above – ascribed to *direct* line fluorescence – and under – ascribed to *indirect* line fluorescence – separately. The error introduced by this separation was small.

In fig. 2 an example is shown of the linear dependence of $I_{\text{dir}}/I_{\text{ind}}$ on $1/p$. From least-squares fits we calculated values for the relaxation rate constants; these values did not systematically depend on the kind of oxidant used, nor on its concentration. Also our measurements with a constant percentage of oxidizer yielded within the error limits the same values – though they are expected to be a weighted average of the rate constants for argon and oxidant. The experimental rate constants spread statistically around the overall weighted averages: $\langle k_r \rangle = (91.3 \pm 1.9) \times 10^3 \text{ Pa}^{-1} \text{ s}^{-1}$ and $\langle k_v + k_q \rangle = (21.0 \pm 0.9) \times 10^3 \text{ Pa}^{-1} \text{ s}^{-1}$; at an estimated temperature of $350 \pm 50 \text{ K}$ this corresponds to averaged cross sections $\langle \sigma_r \rangle = 92 \text{ \AA}^2$ and $\langle \sigma_v + \sigma_q \rangle = 21.2 \text{ \AA}^2$, respectively. This overall cross section for rotational relaxation from the initial $v' = 8$, $J' = 49$ level has the same order of magnitude as those found by Gottscho et al. [11] for $\text{BaO}(A^1\Sigma, v' = 1)$: $\sigma_r = 40 \pm 10 \text{ \AA}^2$ for $J' = 0$ and $\sigma_r = 60 \pm 15 \text{ \AA}^2$ for $J' = 15$.

5. Discussion

Eq. (3) will only be applicable if the overall rate constants for vibrational relaxation and quenching do not depend markedly on the rotational quantum number J' . If they do, $I_{\text{dir}}/I_{\text{ind}}$ would not be a linear function of $1/p$ at higher pressures. In none of our plots can such a deviation from linearity be noticed. Another assumption underlying the derivation of eq. (3) is that no repopulation of the $A^1\Sigma, v' = 8$ state occurs after a vibrationally or electronically inelastic collision. Repopulation after a vibrationally inelastic collision can be ignored, as the fraction of thermal collisions with sufficient energy for a $\Delta v' = +1$ transition (energy defect 500 cm^{-1}) is $\approx 10\%$. At a maximum perturber gas pressure of 200 Pa we estimate, using our measured value for $\langle k_v + k_q \rangle$ as an upper limit, that for the next lower level $v' = 7$ spontaneous decay and (further) downward vibrational relaxation are each at least 10 times likelier than a transition back to $v' = 8$. This is confirmed by experiment as we detected at this pres-

sure only a faint fluorescence from $v' = 9$ and none from higher v' . Collisional repopulation of $v' = 8$ from $v' < 7$ is of course even less probable. For similar reasons repopulation after an electronically inelastic collision does not occur unless the transitions involve only a small change in energy. Because of the Franck-Condon principle this leads in the case of $\text{BaO}(A^1\Sigma, v' = 8)$ to the exclusion of all intermediate states except possibly the metastable $a^3\Sigma$ [17,18]. Collisional mixing between the $A^1\Sigma$ and the $a^3\Sigma$ would then imply a pressure-dependent lengthening of the effective radiative lifetime of $A^1\Sigma, v' = 8$ levels, invalidating the linearity of eq. (3). As stated above, we did not find a deviation from linearity, even at higher pressures. Previous measurements, e.g. by Johnson [10] for BaO° collisions with He in a much wider pressure range of 60 to 2500 Pa, did not show any pressure dependence of the effective radiative lifetime either.

6. Conclusion

The theory derived above enables us to measure rate constants with low resolution and at moderately high perturber gas pressures, i.e. irrespective of the realization of single-collision conditions. Both contribute to a good signal-to-noise ratio and therefore the experimental error improves considerably compared to earlier work [11,12]. It should furthermore be noted that all intensity measurements need only be made *relative* to the direct line intensity.

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References

- [1] Ph. Bréchignac, *J. Phys. (Paris)* **38** (1977) L145.
- [2] Ph. Bréchignac, *Chem. Phys.* **34** (1978) 119.
- [3] M.D. Rowe and A.J. McCaffery, *Chem. Phys.* **34** (1978) 81.
- [4] T.A. Brunner, N. Smith, A.W. Karp and D.E. Pritchard, *J. Chem. Phys.* **74** (1981) 3324.
- [5] S.L. Dexheimer, M. Durand, T.A. Brunner and D.E. Pritchard, *J. Chem. Phys.* **76** (1982) 4996.
- [6] J. Derouard, Thesis, Grenoble (1983).
- [7] Ch. Ottinger, "Méthodes de Spectroscopie sans Largeur Doppler de Niveaux Excités de Systèmes Moléculaires Simples, Colloques Internationaux du CNRS No. 217, Paris (1974) pp. 49-68.
- [8] O. Nédélec and J. Dufayard, *J. Chem. Phys.* **76** (1982) 378.
- [9] T. Wijchers, Thesis, Utrecht (1981).
- [10] S.E. Johnson, *J. Chem. Phys.* **56** (1972) 149.
- [11] R.A. Gottscho, R.W. Field, R. Bacis and S.J. Silvers, *J. Chem. Phys.* **73** (1980) 599.
- [12] S.J. Silvers, R.A. Gottscho and R.W. Field, *J. Chem. Phys.* **74** (1981) 6000.
- [13] Th. G. Cats, J.G.M. Kuerten and H.A. Dijkerman, Eighth Colloquium on High Resolution Molecular Spectroscopy, Book of Abstracts, Tours (1983) paper F15.
- [14] C.Th.J. Alkemade, T.J. Hollander, W. Snelleman and P.J.Th. Zeegers, *Metal vapours in flames* (Pergamon Press, Oxford, 1982) p. 111.
- [15] C.R. Jones and H.P. Broida, *J. Chem. Phys.* **60** (1974) 4369.
- [16] J.B. West, R.S. Bradford Jr., J.D. Eversole and C.R. Jones, *Rev. Sci. Instrum.* **46** (1975) 164.
- [17] R.A. Gottscho, P.S. Weiss and R.W. Field, *J. Mol. Spectry.* **82** (1980) 283.
- [18] R.A. Gottscho, J.B. Koffend and R.W. Field, *J. Mol. Spectry.* **82** (1980) 310.