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Citation: AIP Conference Proceedings **160**, 364 (1987); doi: 10.1063/1.36768
View online: http://dx.doi.org/10.1063/1.36768
View Table of Contents:
http://scitation.aip.org/content/aip/proceeding/aipcp/160?ver=pdfcov
Published by the AIP Publishing

REDUCTION OF 1+1 REMPI SPECTRA TO POPULATION DISTRIBUTIONS: SATURATION AND INTERMEDIATE STATE ALIGNMENT EFFECTS

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ABSTRACT

A two-step methodology is presented for extracting ground state population distributions from 1+1 resonance enhanced multiphoton ionization (REMPI) spectra. In the first step the ion signal is corrected for variation with laser intensity as it is collected, generating an iso-power spectrum. In the second step populations and alignments are derived from the iso-power spectrum by correcting for the interdependent effects of saturation and intermediate state alignment. This procedure is applied to a room temperature thermal distribution of nitric oxide using the 1+1 REMPI process in which lines of the NO $A^2\Sigma^+$-$X^2\Pi$ (0,0) band constitute the resonant transition. The present treatment is able to recover the known rovibrational population distribution, independent of branch choice, over a wide range of practical operating conditions.

INTRODUCTION

Resonance enhanced multiphoton ionization (REMPI) is generally regarded to offer more sensitivity than laser induced fluorescence (LIF) for detecting low concentrations of small gas-phase molecules. In addition, REMPI may be more widely applicable. However, before the benefits of REMPI can be routinely realized in the quantum state analysis of molecular samples, it is necessary to be able to relate unambiguously ion yields to ground state populations. This task is by no means a trivial one, because the REMPI technique is inherently a nonlinear process requiring high laser powers, and hence is more susceptible to saturation effects, power broadening, AC Stark broadening, laser intensity variations, etc.[1]

This paper describes a methodology for reducing 1+1 REMPI spectra to accurate population distributions and alignment factors and applies this procedure to the 1+1 REMPI spectra of the (0,0) band of the NO $A^2\Sigma^+$ - $X^2\Pi$ transition as a test case. Proper spectral reduction is achieved in two steps: first, ion yields are recorded as a function of laser wavelength in a manner such that all ion intensities correspond to the same effective integrated laser intensity; second this so-called iso-power spectrum is then corrected for the combined effects of saturation and intermediate state alignment.

EXPERIMENTAL

The experimental details are more fully described elsewhere.[2] A time-of-flight tube is used for MPI ion collection. The tunable UV radiation (224-227 nm) is generated through Raman shifting the doubled output of a Nd:YAG pumped dye laser.

THE NO $A^2\Sigma^+$-$X^2\Pi$ TEST CASE

A 1+1 REMPI system of choice is the (0,0) band of the NO $A^2\Sigma^+$ - $X^2\Pi$ transition. The intermediate state lifetime has been measured to be 216±4 ns,[3] and the NO A - NO^+ X photoionization cross section as (7.0±0.9) x 10^{-19} cm^2.[4] Total pressures as low as 10^{-11} torr can be detected under tightly focused conditions.[5] Figure 1 shows a typical 1+1 REMPI spectrum of NO recorded at a temperature of 299 K and a pressure of 10^{-7} torr. The subbands arising from each spin-orbit ground state are apparent and each rotational line is readily assigned using the known molecular constants of the NO A and X states.[6]

Figure 2 presents an expanded portion of the 1+1 REMPI spectrum (see dashed box in Fig. 1) taken at three different laser powers. Note the marked change in intensity of the same lines under the three different laser power conditions. It is seen that the power dependence exhibits a functional form that is neither linear nor quadratic in the laser intensity. Moreover, the power variation appears to be different for each line in the spectrum and to vary even across a line profile.

Figure 3 shows the Boltzmann plot (logarithm of the intensity/ line strength vs. the internal energy) of a room temperature spectra recorded using a high laser fluence without adequate power normalization. The resulting branch-dependent temperatures vary over a wide range, and the individual branch contributions do not coalesce. This indicates the need for a more comprehensive data collection/ analysis routine.

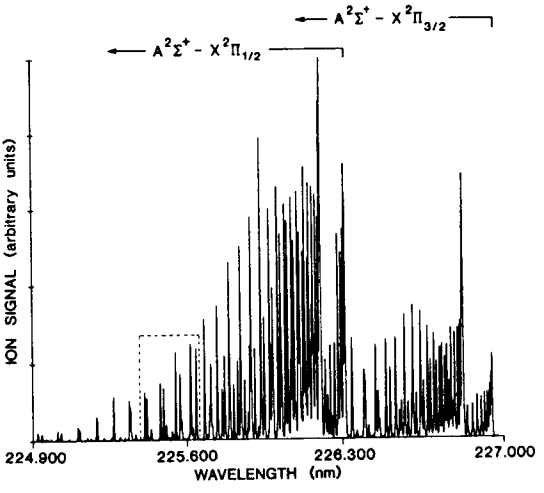

Fig. 1. Thermal(299 K) 1+1 REMPI spectrum of the NO $A^2\Sigma^+$ - $X^2\Pi$ (0,0) band.

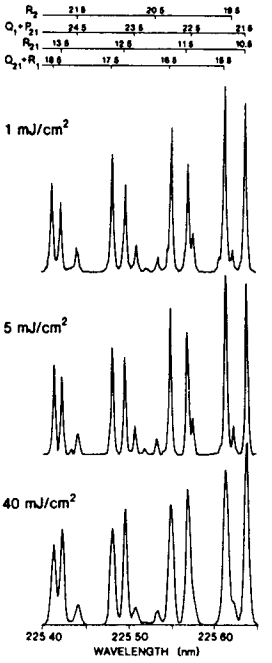

Fig. 2. An expanded portion of the NO $A^2\Sigma^+$ - $X^2\Pi$ (0,0) band [see dashed box in Fig. (1)], recorded under different laser fluences.

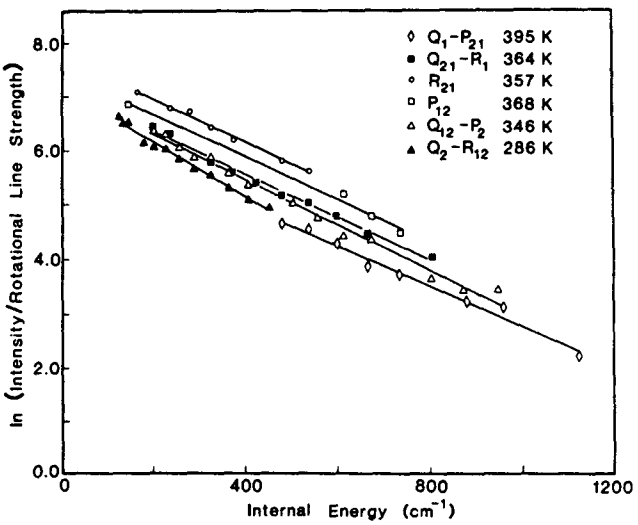

Fig. 3. A Boltzmann plot for an NO 1+1 REMPI spectrum taken under tightly focused conditions (25 cm focal length lens).

METHODOLOGY

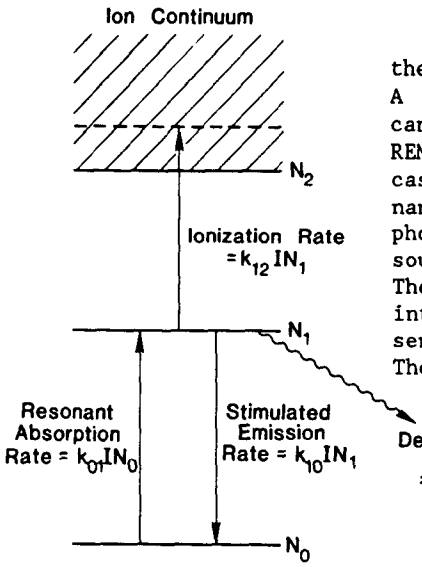

Fig. 4. Schematic Diagram of 1+1 REMPI.

The following draws from the theory presented in detail elsewhere.[7] A simple rate equation model (Fig. 4) can be employed to describe the 1+1 REMPI system. We examine the common case where the two transitions (resonant and ionization) are excited by photons of the same color from the same source, characterized by intensity I. The populations of the ground, resonant intermediate, and ion states are represented by N_0, N_1 and N_2, respectively. The rate constants k_{01}, k_{10} and k_{12} are associated with the processes of resonant absorption, stimulated emission, and ionization. The corresponding rate equations can be analytically solved for the case of a square laser pulse having an intensity I for a duration Δt. The total number of ions produced by the laser pulse can be written as:

$$N_2(\Delta t) = N_0 \left\{ 1 - \frac{1}{2B} \left[(A + B) \exp[-\tfrac{1}{2}(A - B) I \Delta t] - (A - B) \exp[-\tfrac{1}{2}(A + B) I \Delta t] \right] \right\}, \qquad (1)$$

where

$$A = 2k_{01} + k_{12} , \quad (2)$$

and

$$B = (4k_{01}^{2} + k_{12}^{2})^{\frac{1}{2}} . \quad (3)$$

It can be shown that the assumption of a square laser pulse matters little to the final analysis. [7]

Figure 5 illustrates the 1+1 REMPI power dependence for the $R_{21}(10.5)$ line of the NO A-X (0,0) band. Each data point represents the average ion signal for individual laser shots having the specified integrated laser intensity. The saturation function (Eq. 1) fits the data well. It can be seen that linear or quadratic fits are not appropriate for extrapolating the data to an arbitrary integrated laser intensity.

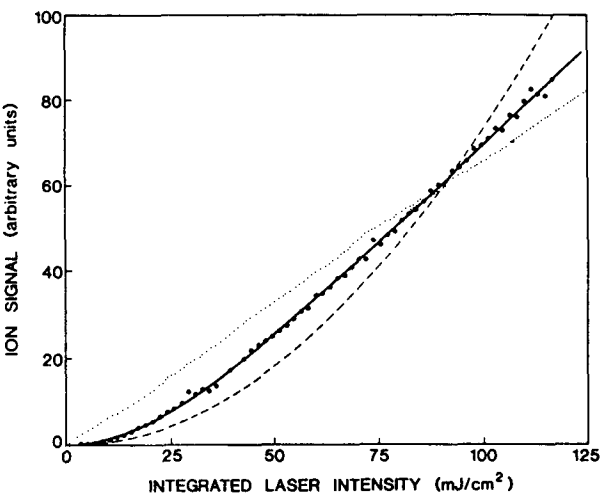

Fig.5. Laser power dependence of the 1+1 REMPI ion signal for the $R_{21}(10.5)$ resonant transition of the NO A-X (0,0) band. The dashed, dotted and solid lines represent the best quadratic, linear and saturation function (Eq. 1) fits to the data, respectively.

During an experimental run, the laser intensity can vary dramatically because of shot-to-shot fluctuations and because of variations in laser gain when scanning across a dye curve. Thus a spectrum must be normalized for laser power changes. The parameters used in the saturation function are expected to change across a wavelength scan. For different spectral transitions, the variations of N and k_{01} correspond to a change in the ground state population and the rotational line strength factor, respectively. At each laser wavelength the ion signal and integrated laser intensity are recorded as data pairs. A group of these data pairs are then fitted in a least squares routine to the functional form of Eq (1) letting N and k_{01} vary. The resulting two parameters (N and k_{01}) may then be used to extrapolate the ion yield to any predetermined constant laser power. This functional fit can be performed at every wavelength point so as to record the spectrum at constant integrated laser intensity. We refer to spectra recorded in this manner as "iso-power spectra".

Figure 6 shows a Boltzmann plot of an iso-power spectra recorded at 20 mJ/cm². Here, the laser power normalized ion yields are simply divided by the resonant transition rotational line strengths $S(J_0, J_1)$, as calculated by a computer program explained elsewhere.[6] The temperature uncertainty represents twice the standard deviation. The

best-fit lines for the various branches do not coincide.

Having recorded a spectrum under iso-power conditions, the problem still remains of correcting for the interdependent effects of saturation and intermediate state alignment. Saturation will affect each branch differently in that the transition strengths for the resonant step are branch dependent, and thus each branch will saturate to a different extent. The intermediate state alignment effect will also show branch dependent variations in the overall ionization efficiency. This latter phenomena can be thought of in the following manner. Suppose a beam of linearly polarized light is incident on an isotropic distribution of ground state molecules (i.e. all M sublevels within a given J are equally populated). The intermediate state will be effectively aligned through the preferential excitation of those molecules having larger projections of the transition dipole moment on the electric field vector of the linearly polarized light beam. Ionization efficiency of the intermediate state can also be M dependent, and thus the degree of anisotropy created in the intermediate state can affect the overall MPI ion production.

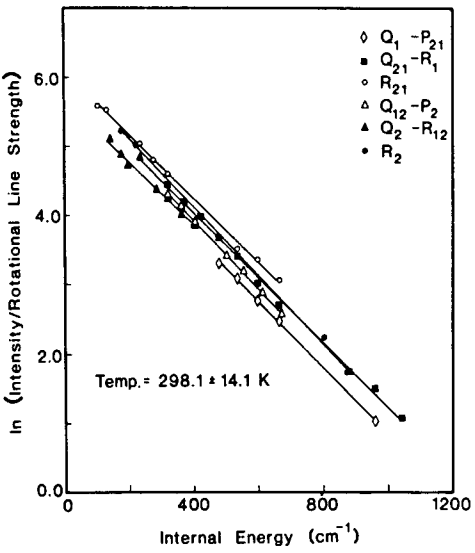

Fig. 6. A Boltzmann plot for the different branch contributions from a 1+1 REMPI spectrum of NO taken under isopower conditions (20 mJ/cm^2).

In order to accomodate these two effects, we choose to follow a quantum treatment, although a classical treatment would have also been satisfactory. Linearly polarized light restricts transitions to follow a $\Delta M=0$ selection rule. This reduces a given transition into a sum of 2J+1 independent transitions. In general, the complete reduction of spectral intensities into relative ground state populations treats each spectral transition probability as a sum over the independent transition probabilities for each M sublevel. Given the M-dependent rate constants, we may utilize Eq. (1) to calculate the saturable ionization efficiencies for each M channel. The total ionization efficiency for a particular transition is then just the sum of the contributions from each M channel.

The M-dependent rate constant for resonant absorption can be written as[7]

$$k_{01}(M) = 3\, C_{01}\, S(J_0,J_1) \begin{pmatrix} J_1 & 1 & J_0 \\ M & 0 & -M \end{pmatrix}^2 , \qquad (4)$$

where $S(J_0,J_1)$ is the normalized rotational line strength factor, and C_{01} is a constant proportional to the Einstein B coefficient.

The M-dependent rate constant for photoionization of an intermediate state, having Σ symmetry, can be written as[7]

$$k_{12}(M) = 3(2N_1+1)(2J_1+1)\frac{\sigma}{h\nu} \sum_{M_S} \begin{pmatrix} N_1 & S & J_1 \\ M-M_S & M_S & -M \end{pmatrix}^2 \sum_{N_2} (2N_2+1) \begin{pmatrix} N_2 & 1 & N_1 \\ M-M_S & 0 & M_S-M \end{pmatrix}^2$$

$$\chi \left[\Gamma \begin{pmatrix} N_2 & 1 & N_1 \\ 0 & 0 & 0 \end{pmatrix}^2 + (1-\Gamma) \begin{pmatrix} N_2 & 1 & N_1 \\ 1 & -1 & 0 \end{pmatrix}^2 \right] \qquad (5)$$

Here, σ is the overall cross section for ionization and Γ is the fraction of parallel character. The quantum number N_2 represents the total angular momentum of the (NO+ + e-) ionization state, excluding spin. Figure 7 illustrates the limiting cases for $k_{01}(M)$ and $k_{12}(M)$.

The fraction of parallel character Γ can be approximated from ab initio calculations;[9] it can also be determined experimentally as a fitting parameter. The fraction of parallel character corresponds to the degree of curvature in the $k_{12}(M)$ distribution. This curvature will dramatically affect the relative ionization probability of P and R compared to Q branches.

A series of iso-power spectra recorded at various total integrated laser intensities can be analyzed together. For each iterative approximation, a trial resonant transition scaling parameter C_{01} and trial Γ parameter are used to produce Boltzmann plots for the entire spectral series. The mean of the uncertainties for the slopes of each Boltzmann plot is minimized by independently varying the values within the parameter set. The final parameter set represents the values of C_{01} and Γ for the system.

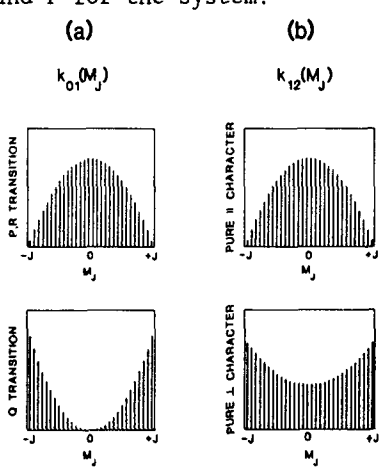

Fig. 7. The M-dependent rate constants for the limiting cases of (a) the resonant transition and (b)the ionization transition.

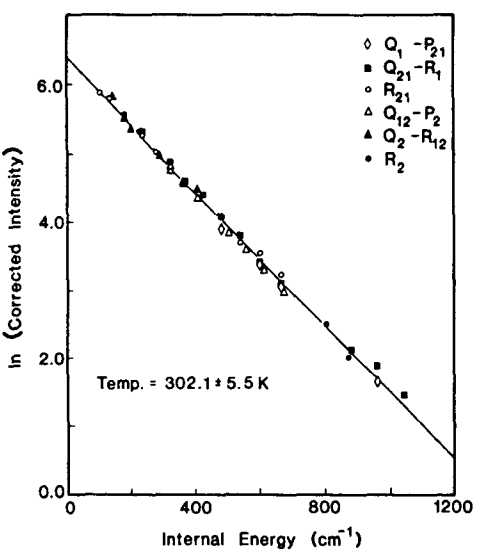

Fig. 8. A corrected (inclusion of intermediate state alignment and saturation) Boltzmann plot for data recorded at an integrated laser intensity of 20 mJ/cm^2

RESULTS AND DISCUSSION

Figure 8 illustrates the corrected Boltzmann plot produced from the same spectral data as that used in Fig. 6. The temperature is found to agree well with the experimental 299 K temperature, and the data points scatter around a common straight line. The proposed methodology improved the precision of measuring a rotational temperature by as much as a factor of 7. The success of the method was demonstrated for laser fluences covering two orders of magnitude. The extracted fraction of parallel character is 44.6% which is in general agreement with the 26.7% calculated by Dixit et al.[9]

ACKNOWLEDGEMENTS

This work was supported in part by Amoco, the National Science Foundation (NSF CHE 85-05926) and the Department of Energy (DE-AT03-79ER10490).

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