

NEW LASER MEASUREMENT TECHNIQUES  
FOR EXCITED ELECTRONIC STATE  
OF DIATOMIC MOLECULES

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Introduction

This paper will briefly outline several new laser measurement techniques which we have developed for the analysis of excited electronic states of diatomic molecules. For molecules which have bound ground states, a visible laser is used to selectively excite a single vibration-rotation level in the electronic state of interest. We then use DC Stark effect, RF double resonance and various fluorescence techniques, as discussed in Sections I and II, to obtain excited state dipole moments, lifetimes, quenching cross sections, transition moments as a function of internuclear distance, and other molecular structure data. We have also developed new laser excitation techniques and used optical double resonance methods for excimer molecules which have repulsive ground states and are bound only in their excited states. These techniques, discussed in Sections III and IV, have been used to obtain potential energy curves,  $f$ - values, lifetimes and various kinetic rates.

I. D. C. STARK EFFECT AND R-F DOUBLE RESONANCE

To determine the dipole moment of electronically excited molecules, an argon ion laser was used to excite the  $C^1\Pi$  state in the NaK molecule, RF and DC electric fields were applied and the resulting fluorescence was analyzed in terms of a fairly straightforward theoretical model.

It was found<sup>(1)</sup> that the 488 nm argon laser line would produce a fairly large population in the  $(v', J') = (7, 24)$  level via the  $(v', J') \leftarrow (v'', J'')$  transition  $(7, 24) \leftarrow (1, 23)$  and the 496.5 nm line populates the  $(7, 5)$  level via the transition  $(7, 5) \leftarrow (4, 5)$ . The  $C^1\Pi$  state of NaK is well described by Hunds case a and each rotational level consists of two closely spaced states of opposite parity ( $\Lambda$  doublets). Since each rotational level in the ground state has a definite parity, the laser induced transition  $(v'J') \leftarrow (v'', J'')$  will excite only one member of the  $\Lambda$  doublet (due to the parity selection rule).

In an unperturbed molecule, the  $J'' = 5$  state gives rise to a  $v''$  fluorescent series of Q lines (the P and R transitions being forbidden by parity) and the  $J'' = 24$  state gives rise to a series of P and R lines. If the excited molecules are perturbed by a weak electric field (10-100 volts/cm) for  $J' = 5$  and a strong field (5000V/cm) for  $J' = 24$ , the  $\Lambda$  doublet states are mixed, some population is transferred to the state of opposite parity, and the parity forbidden transitions begin to appear. Figure (1) shows the fluorescence near 556 nm with the electric

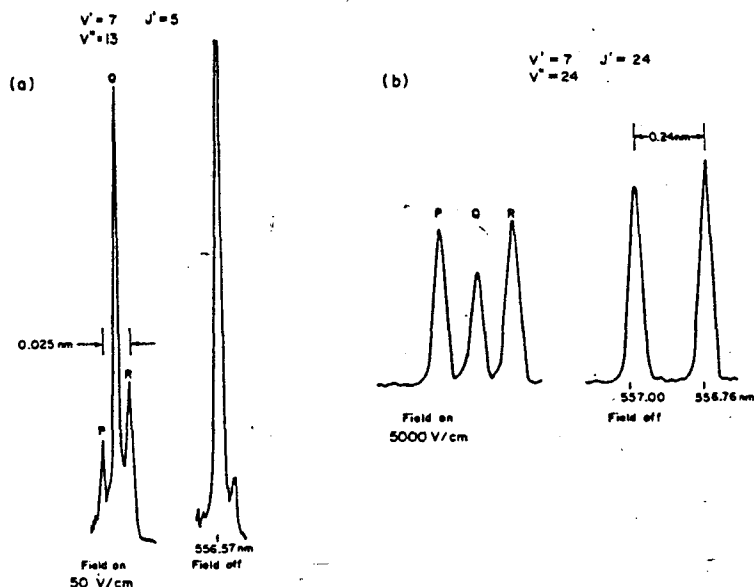


Fig. 1 Effect of Electric Field on Fluorescence Signal for NaK  
(a)  $J' = 5$  (b)  $J' = 24$

field on and off. Figure (2) shows that the intensity of the parity forbidden lines increases with the DC electric field strength until the population in the two states of opposite parity is equalized. A theoretical analysis of this experiment<sup>(2,3)</sup> shows that this intensity is proportional to an expression of the form:

$$I = \sum_M F(M) G(M) X^2(M) / \left[ 1 + X^2(M) \right]$$

$$X(M) = 2\mu EM / \delta J(J + 1)$$

where  $F$  and  $G$  are matrix elements<sup>(2)</sup> that depend on the laser polarization and detector position,  $\mu$  denotes the excited state dipole and  $\delta$  the splitting of the  $\Lambda$  doublet (energy spacing between states of opposite parity). Since the DC electric field strength,  $E$  is known, this measurement provides  $(\mu/\delta)$ ; our statistics indicate that the

accuracy of this ratio is the order of 2%. We measure  $\delta$  by applying an r.f. electric field and sweeping the frequency to find the resonance.

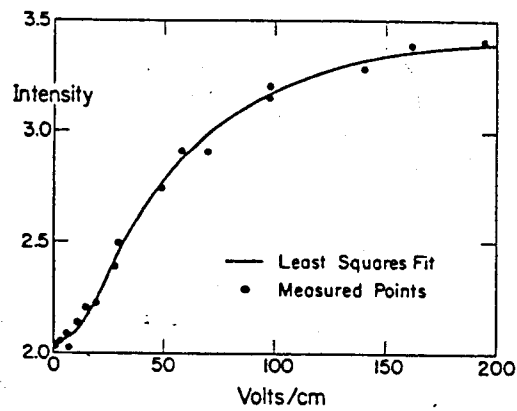


Fig. 2 Intensity of  $J' = 5$  P-Branch of NaK as a function of electric field.

The shape of this resonance signal shown in Fig. 3 is determined by the

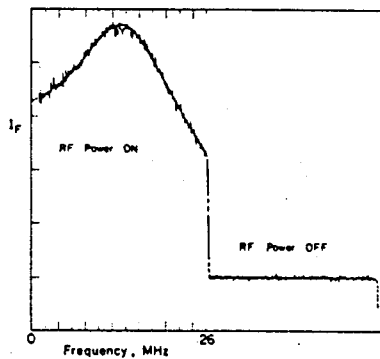


Fig. 3 Resonance signal for  $\lambda$ -doublet splitting of NaK for  $J' = 5$

usual radiative and collisional lifetimes but these data have not yet been extracted since the line is also power broadened by the r.f. electric field; an analysis of these data is currently in progress.

## II. VARIATION OF TRANSITION MOMENT WITH INTERNUCLEAR DISTANCE

Another measurement technique was developed to obtain the variation of the electronic transition dipole moment as a function of internuclear distance<sup>(4)</sup>. The A value for the transition  ${}^1\Sigma_g v''J'' + {}^1\Pi_u v'J'$  is proportional to the square of the matrix element  $\langle v' | R | v'' \rangle$ . We assume that  $R(r)$  can be expanded in powers of the internuclear distance  $r$ ,

$$R(r) = R_0 + \alpha r + \beta r^2 + \dots,$$

the matrix elements  $\langle v' | r^n | v'' \rangle$  are calculated using the known  $\text{Na}_2$  wavefunctions<sup>(5)</sup> and the expansion coefficients  $R_0$ ,  $\alpha$ ,  $\beta$ , etc are determined by comparison with experiment. For example these coefficients may be determined by a least squares fit to the measured lifetimes<sup>(4)</sup>  $\tau_v^{-1} = \sum_{v''J''} A(v'J', v''J'')$  for various vibrational levels. The coefficients  $\alpha$ ,  $\beta$  ... may also be determined by a least squares fit to the intensities  $I(v', v'')$  of a  $v''$  fluorescence series (since  $I$  is proportional to the A value).

To demonstrate this measurement technique, we measured the intensities of two  $v''$  fluorescence series<sup>(4)</sup> excited by the 488 nm and 476.5 nm argon laser lines and used the lifetime data of Baumgartner, Demtroder, and Stock. These three independent determinations of  $R_0$ ,  $\alpha$ ,  $\beta$  gave for the  ${}^1\Sigma_g + {}^1\Pi_u$  transition in  $\text{Na}_2$ ,  $R_0 = 6.8 \pm 0.2\text{D}$ ;  $\alpha = 0.4 \pm 0.1 \text{ D/\AA}$ ;  $\beta < 0.1 \alpha$ . These results are in qualitative agreement with a crude theoretical calculation by Tango and Zare; a more accurate ab initio calculation of  $R(r)$  is currently in progress. Our results disagreed radically with an analysis by Callender, et. al.<sup>(6)</sup> who used a somewhat different technique, but recent changes<sup>(7)</sup> in their analysis have improved the agreement considerably.

## III. EXCIMER MOLECULES - LASER PUMPING FROM THE GROUND STATE

Excimer molecules are of current interest<sup>(8)</sup> as high power laser candidates. These molecules are difficult to study by conventional spectroscopic methods because of their repulsive ground state. Actually many excimers have a small ground state well produced by Van der Waals attraction but this well is so shallow (usually a few hundred  $\text{cm}^{-1}$ )

and lies at such large internuclear distances that conventional absorption spectroscopy provides very little information about the excited states. We have therefore developed new laser measurement techniques for studying this class of molecules; these techniques have been applied to  $\text{Hg}_2$  as an example.

Previous analyses of electronically excited  $\text{Hg}_2$  could be divided into three categories (1) low density (less than  $3 \times 10^{16}$  Hg atoms/cm<sup>3</sup>) optical excitation in which the atomic resonance line is used to excite the  $6^3P_1$  atomic state which then produces excited  $\text{Hg}_2$  via three body recombination. (2) low pressure discharge excitation and (3) high energy (MeV) electron beam excitation at atomic densities greater than  $3 \times 10^{18}$  cm<sup>-3</sup>. The resonance lamp excitation is restricted to low pressures because of optical depth problems and at low pressures the molecular formation rate is quite slow; this rate can be enhanced by adding  $\text{N}_2$  but the presence of a foreign gas complicates the analysis of the  $\text{Hg}_2$  molecular structure and Kinetics. Electric discharge and electron beam excitation are inhibited by the presence of too many lines emitted by highly excited ions and neutrals. We have therefore developed a highly selective laser excitation scheme in which the 253.7 nm mercury resonance line is pumped in the line wing at 257.2 nm using the 15 mW output of a doubled Argon ion laser. There is no optical depth problem in the line wings and we have used this technique to selectively excite the  $6^3P_1$  state at pressures up to several atmospheres where the molecular formation rate is very high. Figure 4 shows a typical laser induced fluorescence spectrum of the  $\text{Hg}_2$  molecule. Two continuous bands are emitted, one centered at 335 nm and the other at 485 nm. For high temperatures ( $T > 575\text{K}$ ) and high densities ( $N > 10^{17}$  cm<sup>-3</sup>) it was found that, for any two wavelengths,  $\lambda_1$  and  $\lambda_2$  in these bands, the ratio of intensities  $R = I(\lambda_1)/I(\lambda_2)$  is an exponential function of temperature of the form  $\exp(\Delta E_{12}/kT)$ . In ref. (19) it was argued that the states emitting these bands are in thermal equilibrium at these high temperatures and densities; a theoretical analysis based on this argument shows that  $\Delta E_{12}$  equals the difference in energy between the states which emit at the wavelengths  $\lambda_1$  and  $\lambda_2$ .

Thus it was possible to map out the potential curves and the f-values for these electronic states by plotting  $\log R$  versus  $1/kT$  for several values of  $\lambda_1$  and  $\lambda_2$ . In addition, from the pressure and temperature dependence of both steady state and time dependent molecular fluorescence the basic kinetics of the pure  $\text{Hg}_2$  system has been analyzed. For further details, see reference 9. The effect of the buffer gases He, Ar, Xe and  $\text{N}_2$  was studied for buffer gas densities ranging from zero to

$10^{20} \text{ cm}^{-3}$  and mercury densities ranging from  $3 \times 10^{16}$  to  $1 \times 10^{20} \text{ cm}^{-3}$ .

Except for some minor changes in diffusion rates there were no observed effects due to the buffer gases when the mercury atom density was greater than  $5 \times 10^{17} \text{ cm}^{-3}$ . Results such as this are very important for  $\text{Hg}_2$  laser design and could not be inferred from low pressure fluorescence data.

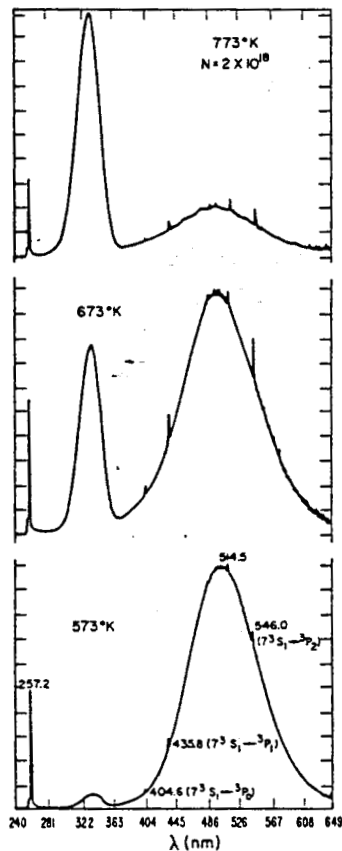


Fig. 4 Mercury fluorescence spectrum at various temperatures for a fixed atomic density of  $2 \times 10^{18} \text{ cm}^{-3}$ .

#### IV. EXCIMER MOLECULES - LASER OPTICAL DOUBLE RESONANCE TECHNIQUE

The above excitation scheme can be used to create a high steady state excimer density (approximately  $10^{12} \text{ cm}^{-3}$ ) in the manifold of states which arise from the  $6^3 \text{P}_0$  and  $6^3 \text{P}_1$  atomic states. This excimer population can then be probed by a second laser to look for

excited state absorption or gain on transitions to the ground state. The excited state fluorescence induced by the probe laser can then be used to map out higher electronic states in a systematic manner. By chopping the probe laser and measuring the phase lag of the excited state fluorescence one can measure various inelastic rates for specific excited electronic states.

Thus far, we have made four types of measurements using this excited state fluorescence technique:

(1) The 15 mW output of the pump laser at 257.2 nm was tightly focused to  $10^{-2} \text{ cm}^2$  and two photon pumping was observed. The second photon apparently excites only repulsive states which dissociate to  $\text{Hg}(7^3\text{S}_1)$  since the only new fluorescence features observed were atomic transitions resulting from that state as seen by the spikes at 404.6, 435.8 and 546.0 nm in Fig. 4.

(2) A 1 watt 488 nm argon laser line was used as a probe laser. The probe laser was chopped and focused to  $10^{-2} \text{ cm}^2$  colinearly with the 257.2 nm pump laser as shown in Fig. 5. The modulated fluorescence signal was measured with a lock in detector and the modulated signal

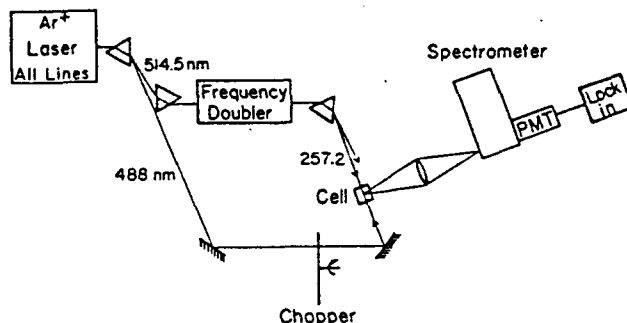


Fig. 5 Experimental setup for optical double resonance experiment.

is given by the dashed curve in Fig. 6 (the solid curve gives the unmodulated fluorescence for comparison); a positive signal corresponds to an increase in fluorescence when the probe laser is on, similarly a negative signal corresponds to a decrease in fluorescence intensity due to the probe laser. The probe laser reduced the fluorescence intensity at all wavelengths except 225 nm, 235 nm, 254 nm and 488 nm. The latter is due simply to the strong scattered light from the probe laser, but, under high resolution, the 225 nm (20 nm wide) and 254 nm (1 nm wide) features prove to be highly structured molecular bands and the narrow emission feature at 235 nm seems to be a Rydberg band. All bands will be analyzed to give molecular constants for the excited states involved.

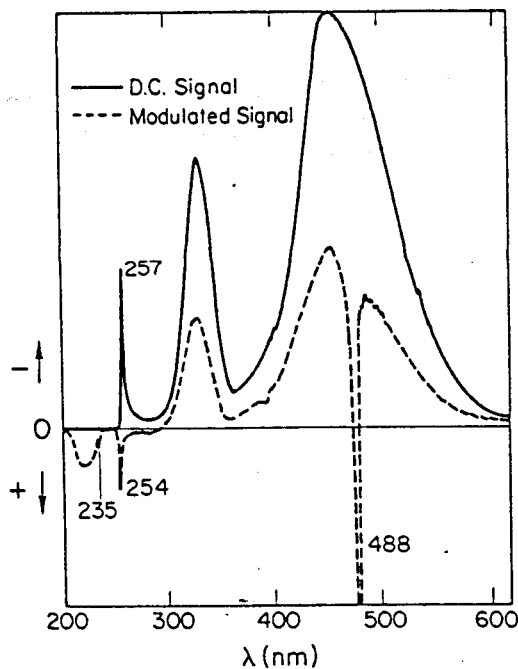


Fig.6 Hg<sub>2</sub> fluorescence signal with and without lock-in detection.

(3) A 1 mW HeCd laser at 325 nm focused to  $10^{-2} \text{ cm}^2$  gave no new fluorescence. Recent ab-initio calculations<sup>(10)</sup> in Mg<sub>2</sub> may be used to infer the structure of corresponding states in Hg<sub>2</sub> and this approach also indicates that there is no excited state absorption near 325 nm. This result is very important since the 335 nm Hg<sub>2</sub> fluorescence band is a serious laser candidate and the presence of excited state absorption in this vicinity would inhibit laser action.

(4) A 1 watt Nd YAG laser at 1.06  $\mu\text{m}$  was focused to  $0.04 \text{ cm}^2$  but no alteration in the steady state fluorescence was produced. This wavelength was tried because our measurements of the Hg<sub>2</sub> molecular structure showed that the two principal fluorescence bands at 335 nm and 485 nm are emitted by electronic states which are separated by  $6500 \text{ cm}^{-1}$ . The presence of nonradiating (gerade) states nearby indicated that the Nd laser might be absorbed off resonance and thereby alter the populations in the states radiating at 335 nm and 485 nm. The null result obtained by this measurement probably indicates that vibrational equilibration rates exceed the off resonance pump rate.

It should be emphasized that all of the above experiments relied on the highly selective nature of laser excitation as well as the high



power density which is obtainable with many visible lasers. As more lasers become available and more new fluorescence techniques are adapted to their use, it will no doubt be possible to obtain a great deal of highly specific data on molecular structure and excited state kinetics for electronically excited molecular states.

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