Title

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DISCLAIMER

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Comment on

TWO-PHOTON SPECTROSCOPY OF N_2: MULTIPHOTON IONIZATION, LASER-INDUCED FLUORESCENCE, AND DIRECT ABSORPTION VIA THE $a''\Sigma_{g+}$ STATE

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Comment on "Two-photon spectroscopy of N_2: Multiphoton ionization, laser-induced fluorescence, and direct absorption via the $a''^1\Sigma_g^+$ state"

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In a recent paper in this journal[1], Lykke and Kay reported a new, highly efficient (2+1) REMPI detection scheme for the detection of N_2, employing the $a''^1\Sigma_g^+$ state. Coincidentally, in our laboratory, we have recently completed some experiments on the same detection scheme. In this comment we would like present some additional information provided by our experimental results.

The laser system used in our experiments operates on three-stage pulse-amplification of the cw output of a Coherent 699-29 Autoscan ringlaser[2], giving about 90 mJ/pulse of linearly polarized visible light with a near transform-limited bandwidth of approximately 52 MHz. Up to 4.5 mJ/pulse of tunable radiation around 202 nm are generated by frequency doubling in KDP and mixing in BBO. Doppler-broadened spectra were recorded by focusing the 202 nm light into a parallel plate ionization chamber containing a mixture of N_2 and H_2, using a 15 cm focal length fused silica lens. In addition, Doppler-free spectra were recorded using a counterpropagating laser beam arrangement in a time-of-flight mass spectrometer.[3] On this apparatus, prior to splitting the laser into two beams of approximately equal power, the 202 nm light was passed through a telescope where the beam

acquired a 5 m focal length. A metering valve was used to admit the N_2 into the time-of-flight mass spectrometer.

The room temperature Q-branch spectrum for the N_2 $a''^1\Sigma_g^+$ <-- $X^1\Sigma_g^+$ transition obtained in the Doppler-free arrangement is shown in Figure 1. In this spectrum, which was recorded at full laser power, the lines are observed to have a FWHM of approximately 2 GHz, due to lifetime broadening of the $a''^1\Sigma_g^+$ state. Line-positions in the Doppler-free spectrum were calibrated against the I_2-standard.[4] Fitting the line-positions yielded a term value of 98840.59(1) cm^{-1} and a rotational constant of 1.98979(3) cm^{-1} for the $a''^1\Sigma_g^+$ state, where the rotational constant for the $X^1\Sigma_g^+$ from ref. 5 was used to calculate the latter value.

A portion of the room temperature spectrum obtained in the parallel plate ionization chamber is shown in Figure 2. The linewidth is approximately 12 GHz, which is well above the calculated Dopplerwidth of 6.9 GHz, and indicates even stronger saturation of the ionization step under the sharper focal conditions in this setup.

Inspection of figures 1 and 2 shows that the O- and S-branch transitions are significantly weaker than the Q-branch transitions. According to Bray and Hochstrasser[6], when using a laser with linear polarization, the two-photon excitation rates in a Σ <--> Σ transition scale as

$$\text{O,S-branch:} \qquad I \propto \frac{J(J-1)}{30(2J-1)} * \mu_s^2 \qquad (1)$$

$$\text{Q-branch:} \qquad I \propto \frac{(2J+1)}{9}*\mu_I^2 + \frac{J(J+1)(2J+1)}{45(2J-1)(2J+3)}*\mu_S^2 \qquad (2)$$

where the isotropic and anisotropic transition moments μ_I and μ_S are given as

$$\mu_I^2 = [\ \mu_{/\!/}\mu_{/\!/}' + \mu_+\mu_-' + \mu_-''\mu_+''\ ]^2 \qquad (3)$$

$$\mu_S^2 = [\ 2\mu_{/\!/}\mu_{/\!/}' - \mu_+\mu_-' - \mu_-''\mu_+''\ ]^2 \qquad (4)$$

Our observation that the Q-branch intensities are more intense than the O- and S-branch intensities by approximately a factor of 500 indicates that the two-photon transition is predominantly isotropic. Similar behaviour was recently calculated for the (0,0) band in the two-photon excitation of H_2 to the $E^1\Sigma_g^+$ state.[7] Further insight into the two-photon transition moments of N_2 is precluded at this moment by the difficulty of assigning a dominant intermediate state in the two-photon absorption proces.

The Q-branch spectrum measured by Lykke and Kay[1] showed an anomalous intensity around J=26 which was correctly interpreted as being due to the presence of a perturbation. In our spectrum (Fig. 2) it is readily visible how the Q(26) transition is split into two components. As yet, no attempt has been made to determine the source of this perturbation.

Acknowledgement

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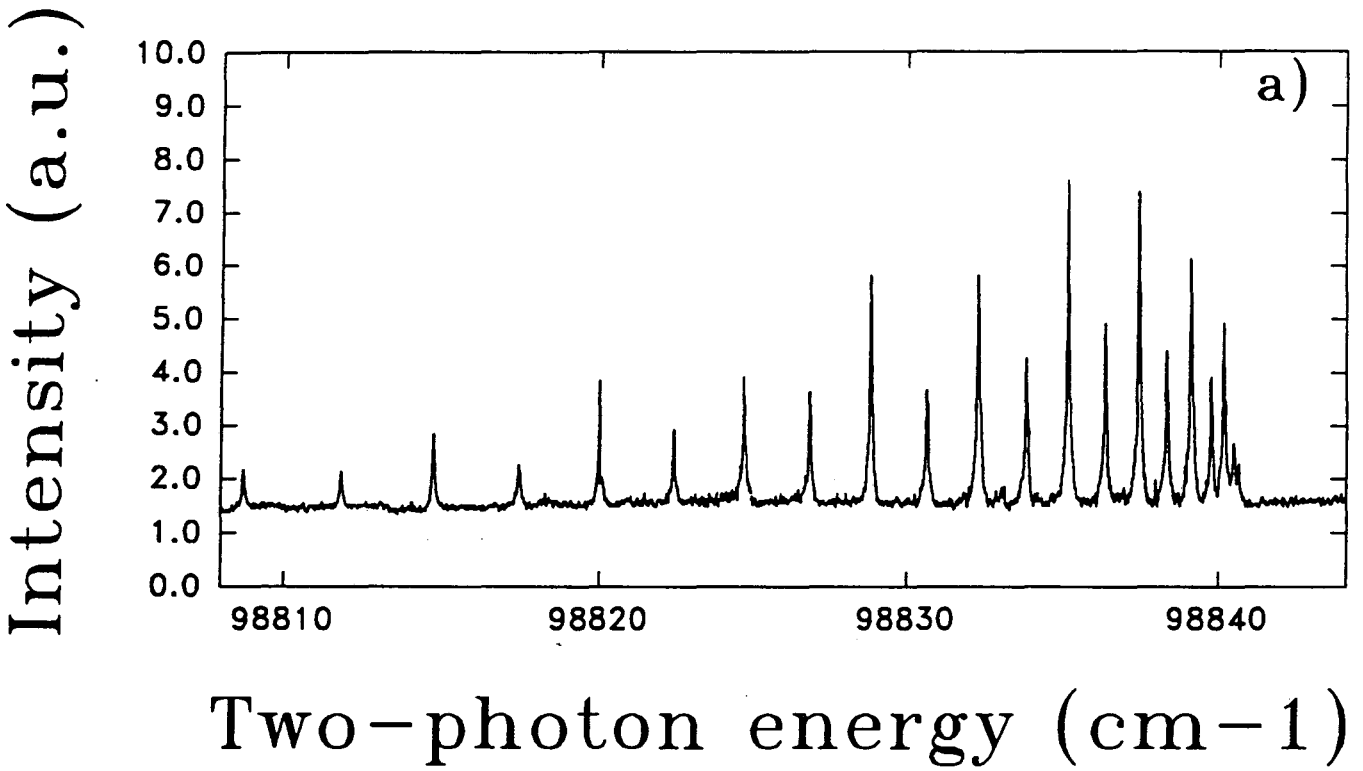
FIGURE CAPTIONS

1. a) Q-branch for the N_2 $a''^1\Sigma_g^+$ <-- $X^1\Sigma_g^+$ ($v_{a''}=0$ <-- $v_X=0$) two-photon transition, obtained using a counterpropagating beam arrangement with a near transform-limited laser.
   b) Portion of spectrum a) near the bandhead of the Q-branch, with full rotational quantum state resolution.

2. Portion of the O-branch and the Q-branch of the N_2 $a''^1\Sigma_g^+$ <-- $X^1\Sigma_g^+$ ($v_{a''}=0$ <-- $v_X=0$) two-photon transition, measured in a parallel plate ionization chamber. An asterisk is placed on the two lines which arise from the perturbation at Q(26).

Doppler-free Q-branch Spectrum



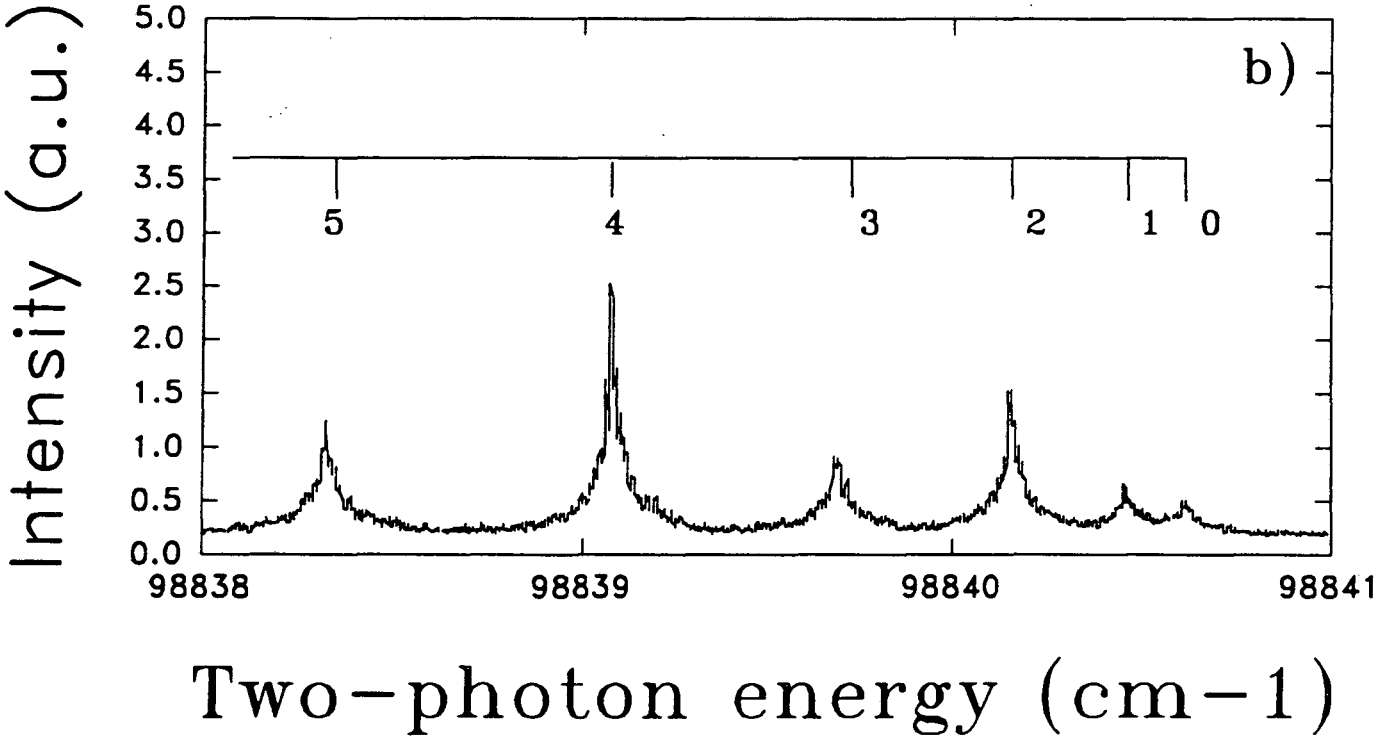


Figure 1

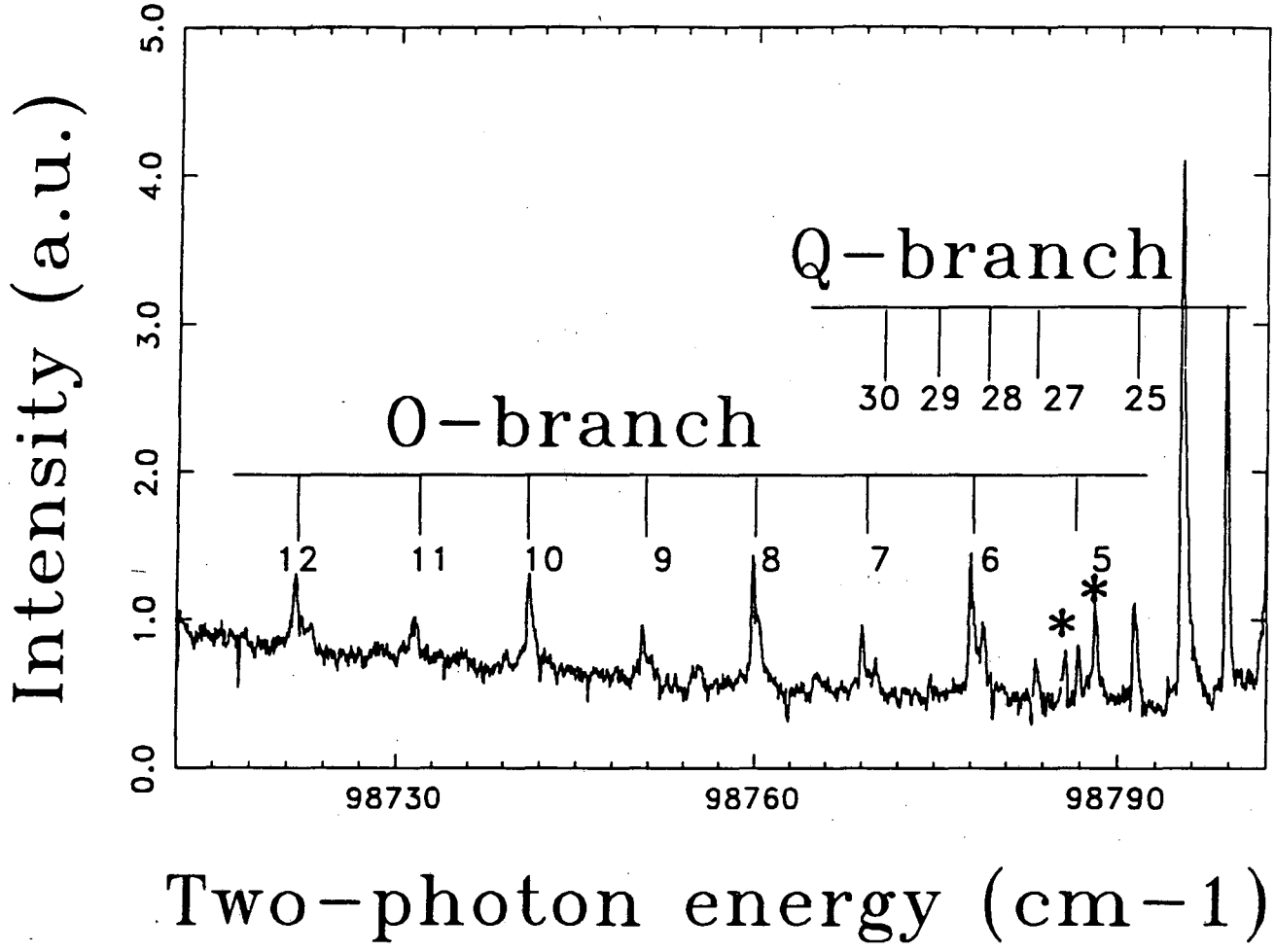

Intensity (a.u.)
0.0
1.0
2.0
3.0
4.0
5.0
Q-branch
30 29 28 27 25
O-branch
12 11 10 9 8 7 6 5
*
*
98730
98760
98790
Two-photon energy (cm-1)

Figure 2

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