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**LETTER TO THE EDITOR**

# Accurate Hartree–Fock vibrational branching ratios in $3\sigma_g$ photoionisation of $N_2$

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**Abstract.** We report vibrational branching ratios for resonant photoionisation of $N_2$ leading to the $X\,^2\Sigma_g^+$ state of $N_2^+$. Our theoretical values are obtained from an accurate solution of the adiabatic-nuclei frozen-core Hartree–Fock model of molecular photoionisation. In contrast to other theoretical results the present results are in very good agreement with experimental measurements. Differences between the present and previous calculations are discussed.

The shape resonance occurring in the photoionisation of molecular nitrogen leading to the $X\,^2\Sigma_g^+$ state of the ion is known to produce significant non-Franck–Condon effects in the final vibrational state distributions. These vibrational effects were first predicted by Dehmer *et al* (1979) and have subsequently been observed experimentally by West *et al* (1980). The original prediction by Dehmer *et al* using the continuum multiple scattering method (CMSM) was qualitatively correct but their computed vibrational branching ratio for the $v' = 1$ vibrational state relative to the $v = 0$ vibrational state was incorrect by approximately a factor of two. Recently Raseev *et al* (1980) have studied vibrational effects in this system using an accurate Hartree–Fock single-centre expansion method. The $v' = 1/v' = 0$ branching ratio reported by Raseev *et al* is in much better agreement with the experimentally measured value of West *et al* (1980) than is the branching ratio obtained by Dehmer *et al* (1979). However, the results of Raseev *et al* are still low by a factor of about 25%.

In the present study we have re-examined the calculations of Raseev *et al* (1980) to determine whether the difference between the computed and experimental branching ratio is due to a breakdown of the adiabatic-nuclei frozen-core Hartree–Fock model used in their study or whether the results given by Raseev *et al* were not fully converged solutions for this model. We have found two deficiencies in the calculation performed by Raseev *et al*. The most important shortcoming of their calculation is that Raseev *et al* only computed the electronic transition matrix elements for three internuclear separations and obtained the value of these matrix elements at all other points using a polynomial interpolation. We have found that it is important to compute the transition matrix elements at more internuclear separations since they are fairly rapidly varying functions of the internuclear separation. Another deficiency of the study of Raseev *et al* is that their potential expansion parameters are not well converged. We know from previous studies (Lucchese *et al* 1981) that with more accurate potential parameters the

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peak photoionisation cross section in the fixed-nuclei approximation for the resonant $3\sigma_g \rightarrow k\sigma_u$ channels of $N_2$ is found to lie at a photon energy of 29 eV rather than at 31 eV as reported by Raseev *et al.* When these two problems are corrected we have found that the adiabatic-nuclei frozen-core Hartree–Fock $\nu' = 1/\nu' = 0$ ratios are in very good agreement with the experimental values of West *et al* (1980).

We have repeated the calculations of Raseev *et al* (1980) correcting the two problems mentioned above. The frozen-core Hartree–Fock approximation was used to describe the interaction between the photoelectron and the ionic core. To obtain the appropriate continuum solutions we have used the Schwinger variational method (Lucchese and McKoy 1980). For the purpose of this study we have not employed the iterative technique which has been applied to other systems (Lucchese *et al* 1980, Lucchese and McKoy 1981), since in our previous studies of the photoionisation of $N_2$ we found that the exact iterative cross section is in general very close to the initial non-iterative result using only $L^2$ basis functions (Lucchese *et al* 1981).

The scattering basis sets we have used for the $3\sigma_g \rightarrow k\sigma_u$ and $3\sigma_g \rightarrow k\pi_u$ photoionisation channels of $N_2$ are given in table 1. These basis sets consist of both Cartesian Gaussian functions defined by

$$\phi^{\alpha,l,m,n,\mathbf{A}}(r) = N(x-A_x)^l(y-A_y)^m(z-A_z)^n \exp(-\alpha|\boldsymbol{r}-\mathbf{A}|^2) \tag{1}$$

and spherical Gaussian functions defined by

$$\phi^{\alpha,l,m,\mathbf{A}}(\boldsymbol{r}) = N|\boldsymbol{r}-\mathbf{A}|^l \exp(-\alpha|\boldsymbol{r}-\mathbf{A}|^2) Y_{lm}(\Omega_{\boldsymbol{r}-\mathbf{A}}). \tag{2}$$

The continuum solutions which are used to obtain the photoionisation cross section are given by

$$\psi^{(-)}_{klm}(\boldsymbol{r}) = \phi^{c(-)}_{klm}(\boldsymbol{r}) + \sum_{\alpha_i,\alpha_j \in R} \langle \boldsymbol{r}|G^{c(-)}U|\alpha_i\rangle [D^{-1}]_{ij} \langle \alpha_j|U|\phi^{c(-)}_{klm}\rangle \tag{3}$$

where $[D^{-1}]_{ij}$ is the matrix inverse of

$$D_{ij} = \langle \alpha_i|U - UG^{c(-)}U|\alpha_j\rangle \tag{4}$$

and where $U$ is the static-exchange interaction potential minus the long range Coulomb potential of the ionic core, $G^{c(-)}$ is the Coulomb Green's function and $R$ is the appropriate scattering basis set given in table 1. All necessary integrals are computed by expanding all functions in truncated partial wave expansions with the resulting radial integrals put on a grid and computed using Simpson's rule. We have also constructed our continuum solutions subject to the constraint that they be orthogonal to the bound orbitals of the same symmetry. More details of this method can be found in previous papers (Lucchese *et al* 1981, Lucchese *et al* 1980, Lucchese and McKoy 1980).

The Hartree–Fock (HF) target wavefunction was constructed from a (9s5p2d/4s3p2d) contracted Cartesian Gaussian basis set (Dunning 1970, Dunning 1971). The computed HF energy of $N_2$ for the equilibrium nuclear separation of $R = 2.068$ au was $E = -108.973\,235$ au, and the quadrupole moment for the neutral $N_2$ molecule in this basis was $-0.9923$ au.

The parameters used to expand the static-exchange potential were as follows:

(i) $l_m = 30$, maximum $l$ included in the expansion of the scattering functions and of the Coulomb Green's function,

(ii) $l_s^{ex} = 30$, maximum $l$ included in the expansion of the scattering functions in exchange terms,

**Table 1.** Scattering basis sets used with the Schwinger variational expression[a].

| Photoionisation symmetry | Type of Gaussian function[b] | | Exponents |
|---|---|---|---|
| $3\sigma_g \rightarrow k\sigma_u$ | Cartesian | $s$ | 16, 8, 4, 2, 1, 0.5 |
| | | $z$ | 1, 0.5 |
| | Spherical | $l=1$ | 4, 2, 1, 0.5 |
| | | $l=3$ | 4, 2, 1, 0.5 |
| | | $l=5$ | 1, 0.5 |
| $3\sigma_g \rightarrow k\pi_u$ | Cartesian | $x$ | 8, 4, 2, 1, 0.5 |
| | | $xz$ | 0.5 |
| | Spherical | $l=1$ | 1.0 |
| | | $l=3$ | 1.0 |

[a] These basis sets correspond to the set $R$ of equation (3) of the text.
[b] The basis functions are symmetry-adapted functions constructed from either Cartesian or spherical Gaussian functions, as defined in equations (1) and (2) of the text, of the type indicated. Cartesian functions are centred at the nuclei and spherical functions are centred at the bond mid-point.

(iii) $l_i^{ex} = 24(1\sigma_g),\ 12(2\sigma_g),\ 12(3\sigma_g),\ 24(1\sigma_u),\ 12(2\sigma_u),\ 12(1\pi_u)$, maximum $l$ included in the expansion of the occupied orbitals in the exchange terms,

(iv) $l_i^{dir} = 30$, maximum $l$ included in the expansion of the occupied orbitals in the static potential,

(v) $\lambda_m^{ex} = 30$, maximum $l$ included in the expansion of $1/r_{12}$ in the exchange terms,

(vi) $\lambda_m^{dir} = 60$, maximum $l$ included in the expansion of $1/r_{12}$ in the static potential.

The grid used to compute all radial integrals consisted of 800 points extending out to $r = 64.0$ au. These potential expansion parameters lead to substantially better convergence than those used by Raseev *et al* (1980).

We have computed the photoionisation transition matrix elements both in the dipole length form

$$I^L_{lm\mu}(R) = (k)^{1/2}\langle \Psi_i(\boldsymbol{r}; R)|r_\mu|\Psi^{(-)}_{f,klm}(\boldsymbol{r}; R)\rangle \tag{5}$$

and dipole velocity form

$$I^V_{lm\mu}(R) = \frac{(k)^{1/2}}{E}\langle \Psi_i(\boldsymbol{r}; R)|\nabla_\mu|\Psi^{(-)}_{f,klm}(\boldsymbol{r}; R)\rangle \tag{6}$$

at five internuclear separations $R = 2.268, 2.168, 2.068, 1.968$ and $1.868$ au. The cross section going from the ground vibrational state of $N_2$ to the $n$th vibrational state of $N_2^+$ is given by

$$\sigma^{L,V}_{\nu=0,\nu'=n} = \frac{4\pi^2}{3c}E\sum_{lm\mu}|\langle \chi_i^{\nu=0}|I^{L,V}_{lm\mu}|\chi_f^{\nu'=n}\rangle|^2 \tag{7}$$

where $\chi$ are the appropriate initial and final state vibrational wavefunctions, $E$ is the photon energy and $c$ is the speed of light. The asymmetry parameter $\beta_k$ is defined from the differntial cross section for the photoelectron by

$$\frac{d\sigma^{L,V}_{\nu=0,\nu'=n}}{d\Omega_k} = \frac{\sigma^{L,V}_{\nu=0,\nu'=n}}{4\pi}(1+\beta^{L,V}_{k,\nu=0,\nu'=n}P_2(\cos\theta)) \tag{8}$$

where $\theta$ is the angle between the direction of the polarisation of the light and the momentum of the electron.

The vibrational wavefunctions were obtained from numerical solution of the Schrödinger equation for the nuclear motion using RKR potentials to describe the potential surfaces. For the $X\,^1\Sigma_g^+$ state of $N_2$ we used the RKR curve of Benesch *et al* (1965). For the $X\,^2\Sigma_g^+$ state of $N_2^+$ we used the RKR curve of Singh and Rai (1966). The values of the potentials between the classical turning points were obtained using six-point polynomial interpolation. The potential curves at $R_e$, 1.097 68 Å for $N_2$ and 1.116 420 Å of $N_2^+$ (Huber and Herzberg 1979), were also forced to have zero slope. The vibrational wavefunctions were then obtained using the method of Cooley (1961). With this approach we obtained the following Franck–Condon factors (FCF): $(\nu = 0, \nu' = 0) = 0.917$, $(\nu = 0, \nu' = 1) = 0.0786$, $(\nu = 0, \nu' = 2) = 0.0043$.

In figure 1 we present the cross section for photoionisation leading to the first three vibrational levels of the $X\,^2\Sigma_g^+$ state of $N_2^+$. We have divided the computed cross section given by equation (7) by the appropriate FCF given above to show the non-Franck–Condon nature of the photoionisation in this spectral region. In figure 2 we present the computed asymmetry parameters and note that they also have a strong dependence on the final vibrational level. In figure 3 our computed $\nu' = 1/\nu' = 0$ branching ratio is compared to the experimentally determined branching ratio of West *et al* (1980) and those of the CMSM model (Dehmer *et al* 1979). From this figure we can clearly see that for photon energies greater than 26 eV the computed ratio is in very good agreement with the measured value of West *et al* (1980). At lower energies the differences are due to the autoionisation features known to be present in the cross section at these energies and which are not included in the present study.

In conclusion we have shown that non-Franck–Condon vibrational effects due to the one-electron (shape) resonance in the photoionisation of $N_2$ can be well represented in the adiabatic-nuclei frozen-core HF model used here. Thus inclusion of electron

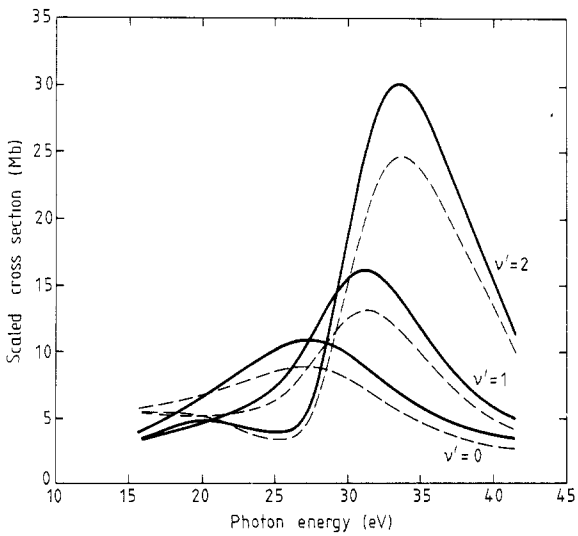


**Figure 1.** Scaled photoionisation cross sections of $N_2$ leading to the $\nu'$ vibrational level of the $X\,^2\Sigma_g^+$ state of $N_2^+$: ——, dipole length approximation; – – –, dipole velocity approximation. The cross sections given here must be multiplied by the Franck–Condon factors given in the text to yield their absolute magnitudes.

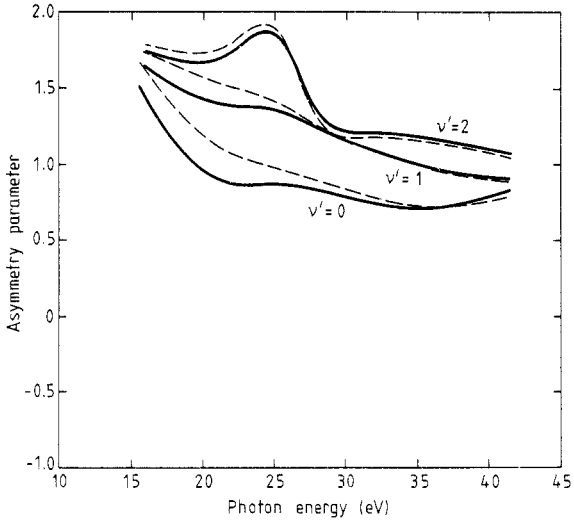


**Figure 2.** Photoelectron asymmetry parameters for photoionisation of $N_2$ leading to the $\nu'$ vibrational level of the $X\,^2\Sigma_g^+$ state of $N_2^+$: ——, dipole length approximation – – –, dipole velocity approximation.

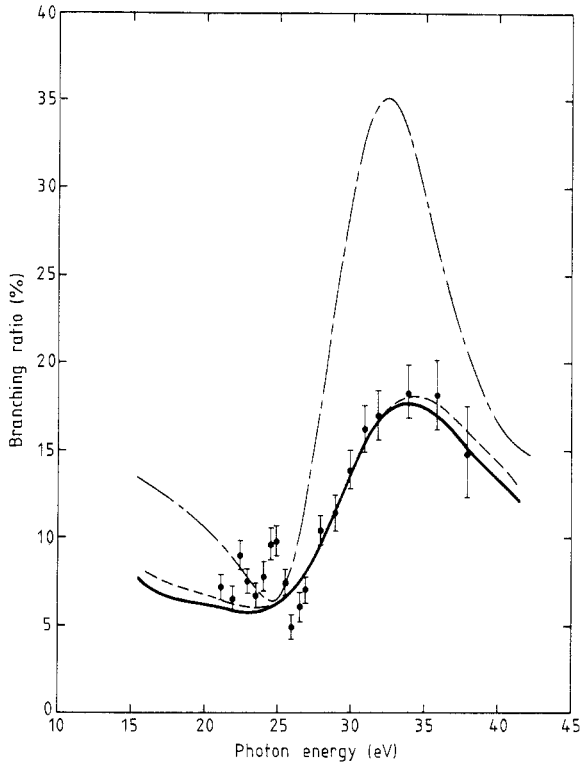


**Figure 3.** Branching ratios for the production of the $\nu' = 1/\nu' = 0$ vibrational levels of the $X\,^2\Sigma_g^+$ state of $N_2^+$ by photoionisation of $N_2$: ——, present results using the frozen-core HF dipole length approximation; – – –, present results using the frozen-core HF dipole velocity approximation ; — · — ·, CMSM results from Dehmer *et al* (1979); ●, experimental results of West *et al* (1980).

correlation effects should change the computed branching ratios very little except in regions where two-electron resonances (autoionisation) are important. Thus the poor quantitative agreement between the CMSM branching ratios and the experimental values (West *et al* 1980) can be attributed solely to an inaccurate representation of the $R$ dependence of the scattering potential in the CMSM model. Moreover, electron correlation effects are probably much smaller than had been anticipated by West *et al* (1980).

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