

Correlation and relaxation effects on the electron-impact excitation of the Lyman-Birge-Hopfield band of N_2

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The behavior of the generalized oscillator strength for the Lyman-Birge-Hopfield transition as a function of the transferred momentum is examined, using the Born-Ochkur-Bonham (BOB) approximation with correlated wave functions. It is shown that the experimental behavior can be well described in the region of small and medium k^2 values, once orbital relaxation and electronic correlation effects are properly taken into account. For large k^2 values the calculations deviate from the experiments due to the failure of the BOB approximation to describe this region.

I. INTRODUCTION

Electron-impact excitation of the N_2 molecule plays an important role in the understanding of auroral and ionospheric phenomena since N_2 is the major atmospheric constituent to altitudes of about 200 km. This process is also important in astrophysics; for instance, in connection with the chemistry of the interstellar medium, the composition of comets, and the opacity of stars.

One of the most studied electron excitation processes, in the N_2 molecule is the dipole-forbidden quadrupole-allowed $X^1\Sigma_g^+ \rightarrow a^1\Pi_g$ transition known as the Lyman-Birge-Hopfield (LBH) band. Despite the large amount of theoretical and experimental effort spent on the characterization of this process, some discrepancies in the generalized oscillator strength (GOS) results still remain.

On the experimental side, GOS results for the large momentum-transfer (k) range were determined by Wong *et al.*¹ at the impact energy of 25 keV, and more recently by Fainelli *et al.*² and Lucas and Souza³ at an impact energy of 1 keV. Lassetre and Krasnow⁴ have also measured GOS for large k values and their results have been revised by Skerbele and Lassetre⁵ for impact energies of 0.3, 0.4, and 0.5 keV. GOS results for the region of small k values were also determined by Odda and Osawa⁶ at impact energies of 0.5, 0.7, 1.0, and 2.0 keV. Several different calculations of the GOS as a function of the momentum transfer have been published. All of them make use of a Born-type approximation for the electron excitation cross section but differ in the description of both the ground and excited states. Theoretical results were obtained through the random-phase approximation (RPA) and the Tamm-Dancoff approximation (TDA) by Szabo and Ostlund⁷ using a minimal basis set of Slater-type orbitals, and by Chung and Lin⁸ in the Born-Ochkur-Bonham (BOB) approximation with Hartree-Fock (HF) molecular wave functions. However, the agreement with experiment is mostly qualitative, and no

calculation describes correctly the behavior of the GOS over the full range of momentum transfer known experimentally. The reason for that could be ascribed to the inadequacy of the Born approximation, to the quality of the wave functions employed in the calculations, or to a combination of both factors.

Chung and Lin⁸ have tested the sensitivity of the calculated GOS, at the HF level, to the choice of the wave function, and concluded that, as long as a reasonable basis set (containing polarization functions) is used, the resulting cross sections would differ typically by about 15%. However, since electron correlation has not been considered in the work of Chung and Lin⁸ and only partially included in the calculations by Szabo and Ostlund,⁷ its effect on the GOS behavior remains to be investigated.

In this work we present the results of a systematic study of the influence of correlation effects on the GOS, using configuration-interaction (CI) wave functions constructed from HF molecular orbitals and considering single to quadruple excitations to the virtual space. Also considered is the effect of direct relaxation as opposed to the frozen-core approximation used in all the previous calculations.

II. COMPUTATIONAL DETAILS

The calculations of the GOS in the BOB approximation were performed using both HF and CI molecular wave functions expanded on the basis of Gaussian-type orbitals (GTO). Starting with Dunning's double- ζ basis,⁹ a modified basis set was constructed which includes s and p diffuse functions as well as d -polarization functions. This basis set was designed with the purpose of studying not only the LBH process but also several other transitions which will be the subject of future work. Its size and range, although limited by our computational capabilities, is such that significant discrepancies between calculated and experimental results cannot be attributed to

TABLE I. Basis set $(12s, 7p, 1d)/[9s, 5p, 1d]$. Exponents above the solid line are contracted together. Coefficients not shown are equal to 1.0.

Basis type	Exponent	Coefficient
s	5909.44	0.002 004
	887.451	0.015 310
	204.749	0.074 293
	59.8376	0.253 364
	19.9981	
	7.1927	
	2.6860	
	0.7	
	0.2133	
	0.1265	
	0.028 00	
	0.011 54	
	p	26.786
5.9564		0.116 407
1.7074		0.390 110
0.5314		
0.1554		
0.052 86		
0.012 95		
d	0.76	

the quality of the basis. The basis set used is shown in Table I. All the calculations were performed at the equilibrium bond distance¹⁰ of 2.068 a.u.

The ground state and the excited state were solved at the HF and CI levels. Two different calculations were performed to obtain the excited-state wave function. In the first one the frozen-core model was assumed, while the second one we solved self-consistently for the excited-state wave function allowing all the orbitals to fully relax.

The CI molecular wave functions for each one of the states considered were obtained allowing single to quadruple excitations from all the respective occupied HF orbitals to a virtual space formed with improved virtual orbitals¹¹ of σ_g , σ_u , π_g , and π_u symmetries. The full CI space (occupied + virtual orbitals) for each one of the calculations consisted of 21 orbitals which generated about 11 000 configurations per symmetry when single to quadruple excitations were considered. Molecular CI wave functions at intermediate levels of excitation (single and single and double) were also obtained.

For the GOS calculations a new computational code was written which allows, in principle, the determination of the GOS for any kind of target (from atoms to large

nonlinear molecules) using either HF or CI wave functions with any degree of correlation. The code also incorporates a biorthogonalization procedure¹² which allows us to compute matrix elements, both at the HF and CI levels, between wave functions built up from nonorthogonal atomic or molecular orbitals. The analytical expression used to compute the GOS, in the Born-Ochkur-Bonhan approximation, is a generalization of the one obtained by Chung and Lin.¹³

In order to reduce the computation time spent for the GOS calculations at the CI level, only configurations which contribute a coefficient greater than 10^{-5} in the original single to quadruple excitation level CI wave functions were considered. This procedure allowed a reduction of the number of configurations from 11 000 to about 1000 per symmetry. The possibility has been considered that configurations which do not contribute appreciably to the variationally determined wave-function energies could still be important when computing the GOS matrix elements. In order to verify this possibility we have considered calculations, at three different points (low, medium, and high k^2 values), which include all the configurations contributing a coefficient as small as 10^{-8} in the CI wave functions. GOS calculations were also performed at intermediate levels of excitation considering only single and single + double excitations.

III. RESULTS AND DISCUSSION

Table II shows the effect of relaxation on the transition energy and also on the GOS results at selected k^2 values. Table III shows the correlation effects on those same properties.

Figure 1 shows the GOS results obtained at different levels of calculation compared to the experimental results.^{2,3} For the sake of comparison we will take the experimental results of Feinelli *et al.*² and Lucas,³ as references because they agree very well with each other and fairly well with those of Lassetre and Krasnow⁴ and Oda and Osawa⁵ in the region of k^2 , where they are available. The reason for the large discrepancy observed between the above-mentioned experiments and the one by Wong *et al.*¹ is planned to be discussed in a forthcoming publication. In Fig. 2 we compare the GOS results of different theoretical calculations^{7,8} with the most recent experimental results.^{2,3}

Several interesting conclusions can be drawn from an examination of Fig. 1. First, regardless of the level of the calculation, the theoretical results reproduce reasonably well the shape of the experimental curve, the maximum of the GOS always occurring at the same value of transferred momentum observed experimentally. Second,

TABLE II. Relaxation effects on the transition energy and generalized oscillator strengths.

Calculation	Generalized oscillator strength				ΔE (eV)
	$k^2=0.066$	$k^2=0.202$	$k^2=0.803$	$k^2=1.425$	
HF (frozen)	0.0130	0.0330	0.0610	0.0530	10.37
HF (unfrozen)	0.0115	0.0294	0.0539	0.0461	10.02
CI single (frozen)	0.0116	0.0293	0.0537	0.0456	10.15

TABLE III. Correlation effects on the transition energy and generalized oscillator strengths.

Calculation ^a	Generalized oscillator strength				ΔE (eV) ^b
	$k^2=0.066$	$k^2=0.202$	$k^2=0.803$	$k^2=1.425$	
HF	0.0115	0.0294	0.0539	0.0461	10.02
CI single	0.0116	0.0296	0.0536	0.0455	9.99
CI double	0.0105	0.0269	0.0499	0.0430	10.66
CI double-quadruple	0.0110	0.0279	0.0514	0.0450	9.87
CI single-quadruple	0.0121	0.0307	0.0556	0.0475	9.80

^aUsing relaxed orbitals.

^b $\Delta E_{\text{expt}} = 9.20$ eV (Ref. 3).

the importance of relaxation effects can be easily inferred from that figure by comparing the results with and without the frozen-core approximation. Relaxation effects can be, of course, introduced indirectly by performing a CI calculation using the frozen-core HF orbitals and including only single excitations, from all the occupied orbitals to the complete virtual space generated by the basis set employed. Therefore we should expect similar results at the unfrozen-core HF level of calculation and at the CI single-excitation level using the frozen-core HF orbitals. From Table II one sees that the transition energies computed at those levels differ by 0.13 eV, while the GOS's are practically indistinguishable.

The importance of correlation effects can be clearly visualized from Fig. 1 and Table III. It is interesting to note that while the best value of transition energy is obtained at the highest level of CI calculation, the GOS values that show the best agreement with experiments are obtained at the CI double or CI double + quadruple level of excitation. To understand the behavior of the GOS it is important to analyze the contributions of the different configurations to the wave functions of each one of the states at the various levels of excitation.

Starting with the relaxed HF orbitals for the excited state, the inclusion of single excited configurations does

not cause appreciable change in the GOS values. This is understandable if we recall that single excitations do not contribute to the ground-state closed-shell wave function and also very little to the excited state obtained self-consistently. Pure correlation effects are observed when doubly excited configurations are considered. In this case one notices a decrease in the GOS values relative to the HF and CI single-excitation results. At the double, triple, and quadruple CI levels of excitation the GOS values approach the HF ones, and when single excitations are also included (single to quadruple), values even higher of GOS are obtained. The examination of wave functions at the CI double to quadruple and CI single to quadruple levels of calculation reveals a strong contribution of the $2\sigma_g \rightarrow 1\pi_g$ excitation. If this last configuration happens to be the dominant one in the description of another electronic state of the molecule, its presence in the CI list could induce some contamination in the GOS value for the transition $X^1\Sigma_g^+ \rightarrow 1^1\Pi_g$. To test this possibility we first performed calculations at the HF (For the $2\sigma_g \rightarrow 1\pi_g$ configuration) and CI levels, and found a state at 31.2 eV, represented dominantly by the $2\sigma_g \rightarrow 1\pi_g$ configuration. We assigned this band to the $X^1\Sigma_g^+ \rightarrow 2^1\Pi_g$ transition. The calculated GOS value for this transition indicates a moderate strong band.¹⁴ These results are in good agree-

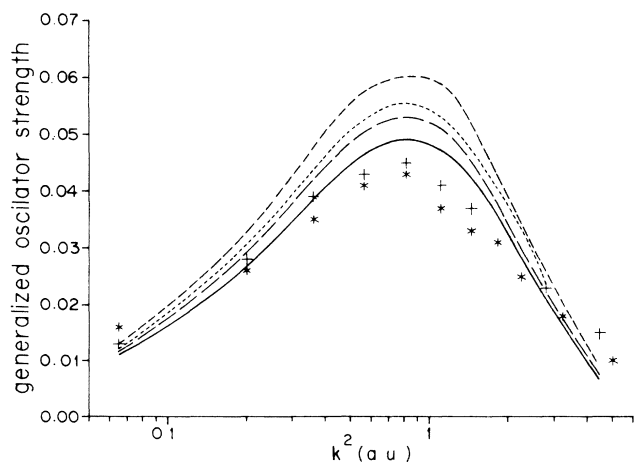


FIG. 1. GOS results at different levels of calculations compared to the experiments: - - -, HF frozen core; - - -, CI single-quadruple; - · - ·, HF relaxed core; —, CI double or double + quadruple; +, Ref. 3; *, Ref. 2.

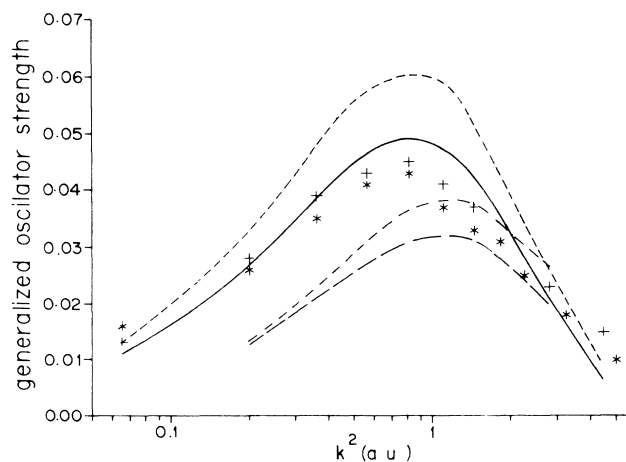


FIG. 2. GOS results of different theoretical calculations compared to the experiments: - - -, HF frozen core, Ref. 8; —, present calculations; - · - ·, TDA Ref. 7; - · - ·, RPA Ref. 7; +, Ref. 3; *, Ref. 2.

ment with the experimental findings of Bonham and co-workers,¹⁵ who observed a transition at 31.4 eV. The authors did not make a definitive assignment of the state but suggested that the band could be related to either intravalence or innervalence excitations. At the CI double to quadruple level of calculation the $2\sigma_g \rightarrow 1\pi_g$ configuration would result from triple excitations made of the combination of the single-excited configuration ($2\sigma_g \rightarrow 1\pi_g$) plus double excitations involving orbitals of a similar nature; for instance,

$$2\sigma_g^2 2\sigma_u^2 \rightarrow 2\sigma_g^1 1\pi_g^1 3\sigma_u^2 .$$

The GOS matrix element between these two configurations will not vanish due to the nonorthogonality of the ground- and excited-state orbitals. The $2\sigma_g \rightarrow 1\pi_g$ single excitation is also present in the excited-state CI single-excitation wave function but due to its small coefficient in the CI expansion ($< 10^{-4}$) no appreciable changes in the GOS values are observed when compared to the HF calculation (Table III). This is consistent with our discussion above regarding the role played by the single excitations alone. Since the excited state has been obtained self-consistently, no orbital shape corrections should be expected from the single excitations. The results that show the best agreement with the available experimental data are the ones obtained at the CI double-excitation level of calculations using the excited-state relaxed orbitals. Although not shown in the figure, GOS values slightly below the CI double-excitation ones have been obtained at the CI double + quadruple level of calculation.

In conclusion, correlation effects are shown to be very important for the correct description of the GOS behavior. The apparent contrary behavior observed when single and/or triplet excitations are included in the CI expansions can be understood in terms of the interaction between the $1^1\Pi_g(3\sigma_g \rightarrow 1\pi_g)$ LBH transition and a reasonably intense ($2\sigma_g \rightarrow 1\pi_g$) transition.

Figure 2 shows the curve obtained at the CI double-excitation level of calculation compared to other theoretical and experimental results. The comparison between our results and the ones by Chung and Lin,⁸ obtained with equivalent basis sets, once more indicates the importance of relaxation and correlation effects on the GOS values. For the sake of clarity we did not plot our HF frozen-core results because they are practically identical to the ones by Chung and Lin. The comparison with the TDA and RPA results of Szabo and Ostlund is also very

instructive. First of all, it is clear from the figure that the GOS values at low transferred momentum are underestimated in the calculations of Szabo and Ostlund.⁷ As the low-momentum collisions mostly probe the diffuse part of the wave functions, the inadequacy of the MBS basis, employed by the authors, to represent the large- r behavior of the states involved, can be inferred. Also, the fact that their GOS values, at the TDA level, are larger than the ones at the RPA level is consistent with the above discussion about the effect of single-excited configurations.

Finally, when compared to the experiments, our calculations show good agreement at low and medium values of transferred momentum. For higher values of k^2 the discrepancies should be most certainly attributed to the failure of the Born approximation to describe this region, as discussed by Huo,¹⁶ than to the quality of the wave functions employed. In this last case higher-order terms in the Born series might be needed to correctly describe the stronger interaction between the incident electron and the target. The small differences between the experimental and the theoretical values, in the region to the left and up to the maximum GOS value, could be due to limitations in the used basis set.

IV. CONCLUSIONS

The behavior of the GOS for the LBH transition, as a function of the momentum transferred, can be well reproduced, in the BOB approximation, once relaxation and correlation effects are properly taken into account. The agreement between theoretical and experimental values, in the region of small and medium k^2 , is good even for the limited, but well-balanced, basis set used in the calculations. For larger k^2 values the discrepancy observed between theory and experiments should be ascribed much more to the failure of the BOB approximation to describe this region than to the quality of the wave functions employed. For large- k^2 values higher-order terms in the Born series might be needed to correctly describe the stronger interaction between the incident electron and the target.

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