Electron-impact excitation of the 31.4-eV band in N_2

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Generalized oscillator strengths (GOS) for the dipole-forbidden 31.4-eV band in N_2 have been determined both experimentally and theoretically. The experimental values for the GOS were obtained using a crossed-beam electron spectrometer at 1-keV impact energy. The theoretical results were determined using the first Born approximation with *ab initio* configuration-interaction target wave functions.

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 sort of 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.

The electronic excitation and ionization of this molecule have been widely studied both by photoabsorption and electron-energy-loss techniques,[1-3] although the overwhelming majority of publications deal with processes occurring below the third ionization potential (*B* state, 18.8 eV). The photoelectron spectrum of this compound, on the other hand, has been obtained[4,5] both with standard x-ray sources and synchrotron radiation over a much wider range, and in particular careful attention has been paid to the inner-valence ionization where several correlation bands point to the breakdown of the independent-particle model.

In 1975 a new band around 31.4 eV energy loss was discovered by Lee, Wong, and Bonham[6] with an electron spectrometer operated at 20-keV impact energy. Generalized oscillator strength (GOS) values were obtained for this band and some possible assignments were discussed. It was shown that its GOS approached zero as the momentum transfer *K* tended to zero, and this band was then associated with a dipole-forbidden process. Similar bands in other molecules were also presented by Lee[7] in a later publication.

Since this process occurs above the third (23.7 eV) ionization potential of this molecule, the intensity observed in electron-energy-loss measurements may be related to all possible processes associated with a particular energy loss. This means, for example, that direct ionization, shakeup, and discrete excitations (independently of the relaxation mechanism followed by the excitation process) may contribute to this intensity and are collected together. As a consequence, several possible processes are candidates for the 31.4-eV band.

As pointed out before, this excitation energy region (23–35 eV) has been widely studied by photoelectron[5,8]

and coincidence (*e*,2*e*) (Refs. 9 and 10) techniques. Several related theoretical calculations have also been performed.[11-17] The inner-valence photoelectron spectra show a complex structure, associated basically with correlation effects. Excitations to virtual states also seem to contribute to the complexity of the photoelectron spectra.

In contrast to the allowed transitions, dipole-forbidden processes above the first ionization potential have only been studied by a very restricted number of authors. Recently, a multiconfigurational time-dependent Hartree-Fock (MCTDHF) calculation was performed by Jaszunski *et al.*[18] in order to characterize the 31.4-eV band.

In the present work the 31.4-eV band is studied experimentally and theoretically. Experimental values for the GOS were determined using a crossed-beam electron spectrometer, at 1-keV impact energy, with an energy resolution of 0.6 eV. Several GOS calculations, using *ab initio* configuration-interaction (CI) target wave functions, were performed in order to discuss the assignment for this band.

II. EXPERIMENTAL SETUP

The experimental setup has been described elsewhere in detail.[19]

The electron-impact spectrometer used for the acquisition of the present data on N_2 consists basically of an electron gun which can be tuned from 500 to 3000 eV, a gas inlet system at 90° with respect to the electron beam (crossed-beam technique), a Möllenstedt[20] electron velocity analyzer, and a conventional detection system.

The energy resolution of the Möllenstedt analyzer is limited by the thermal spread of the electron beam which gives a resolution of about 0.4 eV [full width at half maximum (FWHM)]. The background scattering is reduced by placing a double-slit system (50 and 200 μm) at the entrance of the Möllenstedt analyzer.

The entire system is shielded from the local magnetic field with the use of three pairs of orthogonal Helmholtz coils. These coils reduce the local field from 250 to approximately 2 mG at the scattering center.

The residual pressure is of the order of 10^{-6} torr.

When the gas sample is introduced into the scattering chamber the pressure is raised one order of magnitude. The electron gun, set at 1000 eV, can be rotated from -60 to $+60$ degrees. The Möllenstedt analyzer is swept from 1000 to 950 eV which is equivalent to 50 eV energy loss. For each angle, the spectra are continuously recorded until a good signal to noise ratio is achieved. Figure 1 shows a typical electron-energy-loss spectrum for $\theta = 9\,°$.

The background is corrected by subtracting another spectrum, obtained at the same experimental conditions, but with the gas sample introduced at a side flange, far from the scattering center. The energy-loss scale is calibrated by using the well-known transition $1s$-$2p$ of He at 21.22 eV.

The transmission efficiency of the Möllenstedt analyzer, for this energy, varies according to $E_0/(E_0 - E)$ where E_0 is the primary beam intensity and E is the excitation energy. This correction is performed during data treatment and is known as Kollath correction.[21]

The data were normalized to the absolute elastic cross-section values of Jansen.[22]

The errors are estimated to be as follows:

Errors	Amount
Statistical uncertainty	1.5%
Fluctuations of primary beam current	1.0%
Gas pressure fluctuations	0.5%
Angular uncertainty	20% for $\theta < 4\,°$
	10% for $\theta > 4\,°$
Area of the peaks	20%

Another source of error originates from the normalization procedure when using the elastic cross-section data from the literature.[22] This error is estimated to be 6%. The experimental areas of the peaks are determined by a Gaussian fitting procedure plus exponential tails.

The total uncertainty is estimated to be of the order of 30% for θ below 4° and 25% above this value.
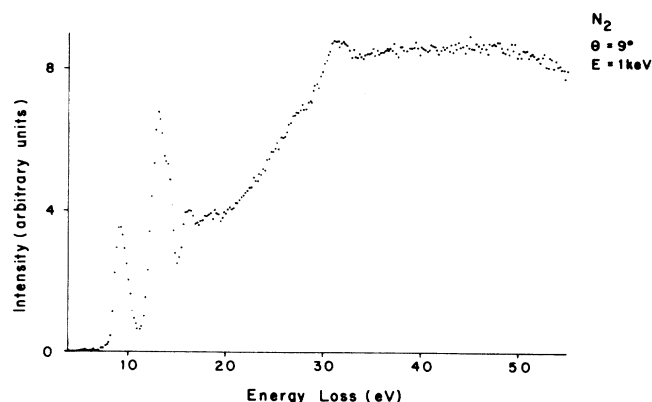

FIG. 1. Electron-energy-loss spectrum for the N_2 molecule obtained at 1 keV and 9°.

III. RESULTS AND DISCUSSION

Several levels of approximations have been employed in the present GOS calculations.

The first level concerns the description of the collision processes, using the first Born approximation. This approximation is expected to describe properly the collision processes[23,24] considering the large impact energy (1 keV) and the small values of the momentum transfer (K).

The target description includes only ground and excited neutral molecular states. This, a priori, excludes the discussion concerning one of the possible assignments to this band as pointed out by Bonham,[25] that is, resonances in the valence ionization channels due to the virtual $3s\sigma_u^*$ and $2p\pi_u^*$ states. This reflects a present limitation in our computational possibilities, that is, it is not possible at the moment to include ionic states in our calculations.

Nevertheless, two facts should be taken into account.

(1) The GOS dependence as a function of K^2 points to a discretelike, dipole-forbidden excitation process (consider, for example, the Lymann-Birge-Hopfield band in the same molecule).[23]

(2) As will be shown, the GOS obtained using only neutral molecular states has already a magnitude similar to the experimental results.

Since correlation effects are known to be important in this portion of the spectrum, the target wave-function calculations were performed both at Hartree-Fock and CI levels. The molecular orbitals were determined from an ab initio code, using an $[(11s,7p,1d)/(9s,5p,1d)]$ Gaussian basis[23] which includes diffuse and polarization functions.

For the ground state $(X\,^1\Sigma_g^+)$ CI wave function, single and double excitations were considered from all the occupied orbitals to a virtual space composed of 14 virtual orbitals of σ_g, σ_u, π_g, and π_u symmetries. The virtual orbitals were generated using the improved-virtual-orbitals (IVO) technique of Hunt and Goddard[26] as excitations from the $3\sigma_g$ molecular orbital.

Among the final symmetries that could give rise to the dipole-forbidden 31.4-eV band, some HF calculations indicated the $^1\Pi_g$ as the most probable. This includes the $2\sigma_g \rightarrow 1\pi_g$ excitation already pointed out[6,25] as the strongest candidate for this band in a monoelectronic description. Our Hartree-Fock calculations, indeed, gave an excitation energy of 31.2 eV for this process, as compared to the experimental value of 31.4 eV.

Previous calculations[23] for the dipole-forbidden Lymann-Birge-Hopfield process indicated that relaxation effects may give rise to significant changes in the calculated GOS values. One should expect these effects to give a larger contribution in our case, since it is related to an inner-valence excitation process. These effects were explicitly taken into account in the present calculations by allowing the core orbitals to relax in the excited state wave function. As a consequence, the occupied and IVO orbitals for the ground and excited state wave functions were no longer mutually orthogonal. The GOS was then calculated using a biorthogonalization procedure described elsewhere.[23,27]

For the excited state $(^1\Pi_g)$ CI wave function,

the 14 IVO's (Ref. 26) were generated as excitations from the $2\sigma_g$ orbital, from a HF calculation of the $2\sigma_g^{-1}1\pi_g$ state, where all the molecular orbitals were optimized. Single and double excitations from the occupied orbitals to all the 14 IVO's were considered, except for the following single excitations from valence orbitals: (i) $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^1 n\pi_g^1$, $n \geq 2$; (ii) $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^3 3\sigma_g^2 n\sigma_u^1$, $n \geq 3$; and (iii) $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^1 1\pi_u^4 3\sigma_g^2 n\pi_u^1$, $n \geq 2$.

These configurations correspond to Rydberg series with excitation energies below 20 eV and were not included in the CI single and double (SD) calculation because of a technical limitation. These configurations lead to CI roots with lower energy than the ones in which we are interested and consequently appear first in the CI calculation, making imprecise the calculation of roots with higher energies. On the other hand, disregarding these configurations in the CI SD calculations does not significantly affect our calculations since they correspond to states with much lower excitation energies which should not contribute to the CI root associated with the excited state around 31 eV. In order to further guarantee that our excited state is orthogonal to the CI root representing the $a\,^1\Pi_g$ state (which leads to the strong Lymann-Birge-Hopfield process), the corresponding valence single excitation configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^1 1\pi_g^1$ was included in the CI calculations.

In the CI calculations for the excited state a CI root with dominant $2\sigma_g \rightarrow 1\pi_g$ character plus some contribution from double excitations was found, with an energy difference with respect to the ground (CI) state of 33.9 eV, a value somewhat larger than the experimental result. This disagreement should be expected, firstly because the ground state is better described (all single and double excitations allowed) than the excited one. A second reason is related to the existence of CI roots with lower energy than the root with $2\sigma_g \rightarrow 1\pi_g$ dominant character. Since the CI roots are orthogonal, this should lead to a poorer description of the root we are interested in.

Our result agrees well with the recent results of Jaszunski et al.,[18] who found, in MCTDHF calculation, a state with the same characteristics described above, at an excitation energy of 33.03 eV. In the work of Jasuzunski et al.,[18] another state of Π_g symmetry was found, with an excitation energy of 31.5 eV, corresponding to a mixing between $1\pi_u \rightarrow 3\sigma_u$ and $1\pi_u \rightarrow \sigma_u$(diffuse). Since in our previous calculation the virtual space did not contain enough diffuse σ_u IVO's, a special calculation with the $3\sigma_u$ and six diffuse σ_u IVO's was performed in order to check for this possibility. The IVO's were generated from a $1\pi_u^{-1}3\sigma_u$ HF calculation. We did not find any CI root with $1\pi_u \rightarrow 3\sigma_u$ and $1\pi_u \rightarrow \sigma_u$(diffuse) characteristics around 31.5 eV. The disagreement may be due to relaxation effects that were not included explicitly in the MCTDHF calculations of Jaszunski et al.[18]

Figure 2 shows the present experimental and theoretical GOS results as a function of K^2 together with the experimental results of Lee, Wong, and Bonham.[6] The two sets of experimental data agree well within the experi-
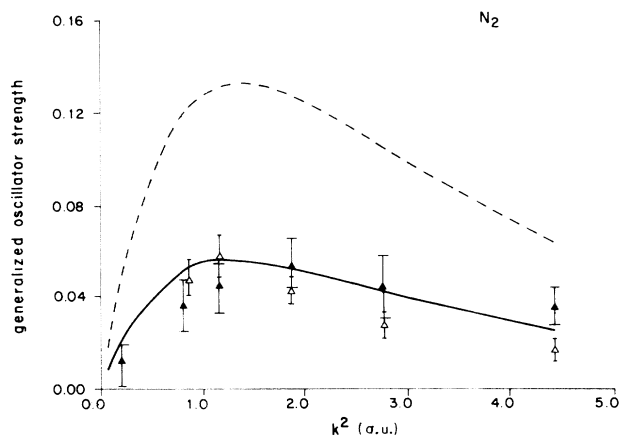

FIG. 2. Generalized oscillator strength (dimensionless units) for the excitation of the 31.4-eV band in N_2. ▲, experimental data of Lee, Wong, and Bonham (Ref. 6); △, present results; — — —, Born-HF; ——— , Born-CI.

mental bars. Both results imply that the 31.4-eV band can be correlated to a quadrupole allowed transition.

The theoretical GOS values obtained with the HF, molecular wave functions are about 2.5 times larger than the experimental ones. As the core orbitals were allowed to relax in the excited state wave function, and a reasonably large basis set was used, the discrepancy between the experimental and theoretical HF results for the GOS cannot be associated to a low-quality HF calculation, but to a failure in the monoelectronic description of the final state, that is, to the noninclusion of correlation effects.

Figure 2 shows very clearly that a good general agreement between the experimental and theoretical results is obtained when CI wave functions are used. A large difference between the GOS values obtained with HF and CI wave function is observed. These results show that correlation effects are also important for discrete inner-valence excitations, in agreement with the expected importance of correlation effects for inner-valence photoionization process. In our case, a strong correlation is found between the single excitation $2\sigma_g^{-1}1\pi_g$ and double discrete excitations.

Of course, the limitations in the CI calculations for the excited state, where the continuum is not actually represented, make the present results incomplete. Nevertheless, the agreement with the experimental data indicates that the present assignment should be close to the exact one.

ACKNOWLEDGMENTS

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