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Valence Resonance States of N_2^-*

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Resonance valence excited states of N_2^- are calculated and used to interpret resonant excitation of the A and B states of N_2 by electron impact.

Key words: Electron scattering resonance; excited states N_2; excited states N^-; inelastic scatter; N_2^-; valence excited states.

Sanche and Schulz [1][1] have observed structure in transmission of electrons between 9 and 11 eV in collision with N_2. They attributed the origin of this structure to the excitation of an unknown state or to resonance phenomena involving attachment of the scattered electron to an excited valence state. The latter interpretation has been supported by recent studies by Mazeau et al. [2], on the resonant excitation of the $A\ {}_3\Sigma_u^+$ and $B_3\Pi_g$ states of N_2.

This note reports calculations of valence negative ions states that will support a valence resonance state mechanism for the observations. The dominant molecular orbital configurations of the $A\ {}^3\Sigma_u^+$ and $B^3\Pi_g$ states are, respectively:

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^3 1\pi_g, \qquad A\ {}^3\Sigma_u^+$$

and

$$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^1 \pi_g, \qquad B^3\Pi_g.$$

Within the $V = 0$ turning points of $X\ {}^1\Sigma_g^+$ there is only one valence excited molecular orbital determined by calculation, the $1\pi_g$. Rydberg attachments are calculated to yield higher energy states and can not be considered within the bound state formalism used in this study; variationally the diffuse electron wave function is found to be a constant and represent a zero-energy continuum electron. But the valence electron is found to be stabilized and an approximation to the resonance state is found by adding a $1\pi_g$ electron to the $A\ {}^3\Sigma_u^+$ and $B^3\Pi_g$ parent configurations to yield (ignoring the core electrons):

$$3\sigma_g^2 1\pi_u^3 1\pi_g^2, \qquad {}^4\Pi_u, {}^2\Phi_u, {}^2\Pi_u(3)$$

and

$$1\pi_u^4 3\sigma_g 1\pi_g^2, \qquad {}^4\Sigma_g^-, {}^2\Delta_g, {}^2\Sigma_g^-, {}^2\Sigma_g^+$$

Three of the lowest energy states were chosen, $^4\Pi_u$, $^2\Phi_u$, and $^4\Sigma_g^-$ and the energy calculated with an all-valence multi-configuration self-consistent-field (MC–SCF) trial function [3]. This procedure was used previously for a study of O_2^- excited states where details may be found [4]. Diffuse trial functions were included for the representation of the $1\pi_g$ function but were not found to dominate the orbital at any distance. This choice of trial wave function restricts the orbitals to be essentially valence in character with, however, the diffuse tail found in atomic negative ions. Since the $N^-(^3P)$ state is not bound the ion asymptotic energies are calculated above the $N(^4S)+N(^4S)$ asymptote. Specific correlation functions are known to correct this error [5] but were not considered since a qualitative survey was felt to be sufficient at this time.

The energy curves are given in figure 1 with the asymptotes shifted to agree with the experimental values. The binding of $N^-(^1D)$ relative to $N(^2D)$ was calculated at the all-valence MC–SCF level without correlation. The $^4\Pi_u$ energy curve has an energy minimum near 1.5 Å (the exact value can not be determined from the relatively few calculated points) and a dissociation energy about 3.2 eV in this approximation. The T_e relative to $X\ {}^1\Sigma_g^+$ is then about 6.8 eV. The $^2\Phi_u$ state has a similarly shaped energy curve that goes asymptotically to $N^-(^3P)+N(^2D)$. It would have a T_e of about 8.5 eV.

The $^4\Sigma_g^-$ curve equilibrium internuclear separation is at somewhat shorter distances than that of the $^4\Pi_u$ state. Estimating the T_e is complicated by the uncertainty in the $N^-(^1D)+N(^4S)$ asymptote. Using the calculated asymptotic energy, the $^4\Sigma_g^-$ T_e is about 8.8 eV.

The $^4\Pi_u$ state is hypothesized to support the A state resonances reported by Mazeau et al. [2], while the

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[1] Figures in brackets indicate the literature references at the end of this paper.

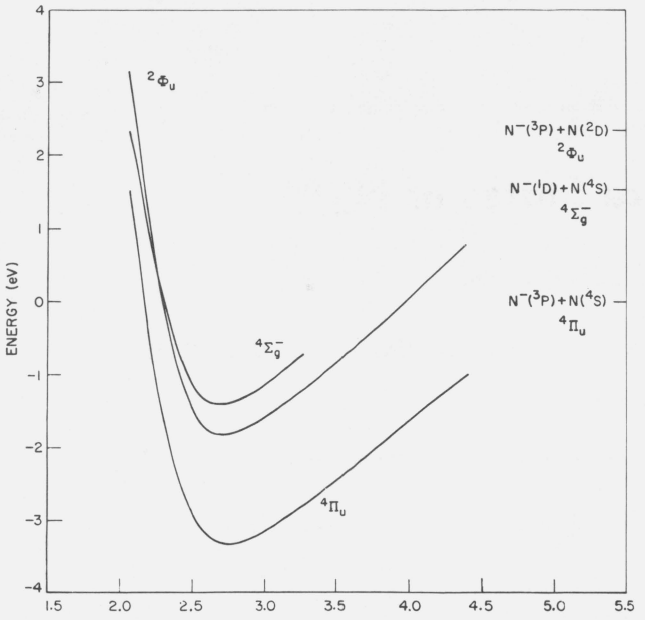

FIGURE 1. *Multiconfiguration electronic energy curves of* N_2^-.

The energy ordinate is given in eV and the internuclear distance on the abscissa is given in atomic units where 1 a.u. equals 0.529177Å.

$^4\Sigma_g^-$ state supports their B state resonances. This agrees with the assumption of Mazeau et al. that these are core excited shape resonances in which the A state parent resonance decays into the A state and similarly for the B state parent resonance. However, these calculations suggest, as observed before [1], that the excited molecular orbital supporting a shape resonance is a valence-type orbital which is the $1\pi_g$ in this case. It is also found that these resonance states are not bound in the Franck-Condon region relative to the parent excited state as noted earlier for valence resonance states [6].

The decay mechanism for these states must be somewhat complicated. This is because both resonance states are quartets which can not be excited from the X $^1\Sigma_g^+$ state without involving a spin-orbit coupling of some kind. The doublet states that can arise are calculated too high in energy to fit the observed excitation energies.

However, $^4\Pi_u - ^2\Pi_u$ spin-orbit mixing provides a means of coupling the ground with the resonance state. The characteristic of the $^2\Pi_u$ state with respect to its auto-detachment width and the depth of its energy curve is not known and renders further analysis difficult.

The mixing of the $^4\Sigma_g^- - ^2\Sigma_g^-$ states is of no concern since the $^2\Sigma_g^-$ state is not reached by electron scattering from the ground state. It is, however, possible to mix the $^4\Sigma_g^-$ and $^2\Sigma_g^+$ states, as well as the low energy $^2\Pi_g$ shape resonance by spin-orbit interaction.

Since the equilibrium internuclear separations of both the $^4\Pi_u$ and $^4\Sigma_g^-$ states are significantly shifted with respect to the neutral ground state, a large number of vibrational levels are expected to be excited. The $^4\Pi_u$ resonances would be apparent only to the dissociation limit of 9.6 eV. In the case of the $^4\Sigma_g^-$ resonance the dissociation limit is $N^-(^1D)+N(^4S)$ which is calculated to be about 1.5 eV above the $N^-(^3P)+N(^4S)$ asymptote. The B resonances are apparent only to 11.15 eV [2] which is remarkably close to the calculated $^4\Sigma_g^-$ dissociation limit. Although the comparison of calculated and observed resonance energies are in reasonable agreement, it should be noted that a fairly complex angular behavior of the scattered electron has been observed and interpreted as due to several resonances [2]. Bound state calculations such as these reported here, however, are mute with regard to the direct scattering process. One should only conclude that the $^4\Pi_u$ and $^4\Sigma_g^-$ states are an important part of the resonant scattering and would have to be included in any more complete treatment.

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