Resonances in the Metastable Excitation of Molecular Nitrogen*

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The excitation function for metastable molecular nitrogen has been studied over the electron-impact energy range 7–14 eV with an energy resolution of 0.05 eV. No resonances were observed below 11.8 eV in the $A\,^3\Sigma_u^+$ and $a\,^1\Pi_g$ channels. There is a sharp resonance at the threshold of the metastable $E\,^3\Sigma_g^+$ with a peak at 12.00 eV. Smaller structures were seen at 12.14 and 12.25 eV. A series of five resonances were observed at 12.59, 12.80, 13.03, 13.24, and 13.52 eV presumably in one or both of the $A\,^3\Sigma_u^+$ and $a\,^1\Pi_g$ channels. These confirm some of the structures observed in a recent transmission experiment. On the basis of the spacings and relative intensities of these resonances, a possible assignment for them is a temporary state of N_2^- consisting of two Rydberg electrons around a core state $A\,^2\Pi_u$ of N_2^+.

I. INTRODUCTION

Excitation effects in molecular nitrogen are of importance, particularly with regard to phenomena in the upper atmosphere. In recent years several measurements have been made of the electron-impact metastable excitation functions,[1–3] and in addition estimates of absolute cross sections and radiative lifetimes for the metastable states have become available. This paper reports the first attempt to study the metastable excitation functions with sufficient electron-energy resolution and detection sensitivity to fully explore the resonant effects. Comparisons are made with results obtained in elastic-scattering,[4] vibrational-excitations,[4] transmission,[5,6] energy-loss,[6,7] and trapped-electron experiments.[8]

II. METHODS

Electrons from a hemispherical monochromator[9] entered a scattering chamber containing N_2 gas at a pressure of about 10^{-4} Torr. Typical incident currents were 10^{-8} A with a resolution of 0.08 eV and 10^{-9} A with a resolution of 0.04 eV. Metastable molecules, excited in inelastic collisions, were detected by the release of Auger electrons at the cathode of a channeltron multiplier. Scattered electrons were prevented from reaching the detector by means of a pair of grids which provided biasing and electrostatic shielding from the scattering chamber. The output of the channeltron, after pulse amplification and discrimination, was integrated by a count-rate meter and displayed on an *XY* recorder. The integrating time was 10 sec and a typical sweep speed for the impact energy was 5 eV/h.

This technique was similar to that used in previous work on metastable excitation of rare gases,[10] except that the incorporation of the electron multiplier greatly enhanced the sensitivity and flexibility of the detection system. The method was sensitive also to uv emission, and for most detector surfaces the quantum efficiency for detection of photons of a given energy is comparable to the Auger efficiency for electrons released by metastable molecules having the same excitation energy. In the 8- to 14-eV range of impact energies, however, the relative contribution of uv photons was small. It is worth noting that this is not the case for the isoelectronic molecule CO, where uv emission is influenced by sharp resonances at thresholds.[11,12] In nitrogen the major contribution to the uv spectrum is from the excitation of the $b\,^1\Pi_u$, with a threshold at 11.55 eV (Lyman–Birge–Hopfield bands). This state is not strongly excited at threshold, as evidenced by trapped-electron[8] and energy-loss[6] experiments. The metastable $a\,^1\Pi_g$ and $A\,^3\Sigma_u^+$ radiate weakly, but in our experiment the uv photons from these states contributed little compared with direct detection, since the 20-μsec transit time from scattering region to detector was far smaller than the radiative lifetimes involved.[13,14]

III. RESULTS

The over-all excitation function is shown as the solid line (a) in Fig. 1 with an energy resolution of about 0.08 eV. Typical detector intensity in counts/sec is illustrated on the vertical scale. The broken-line curves are the data of Borst,[1] the upper one (b) being the total metastable excitation function, and the lower three the contributions from the constituent states $A\,^3\Sigma_u^+$ (c), $a\,^1\Pi_g$ (d), and $E\,^3\Sigma_g^+$ (e). The separation was achieved by time-of-flight techniques, and the vertical scale relative to ours is arbitrary. Our energy scale was calibrated to an estimated accuracy of 0.03 eV, by comparison with the 19.82-eV threshold for excitation of metastable helium.[10] The horizontal scale of the Borst data is an independent calibration. The similarity of our excitation function with that of the lower-resolution work confirms our assumption concerning the

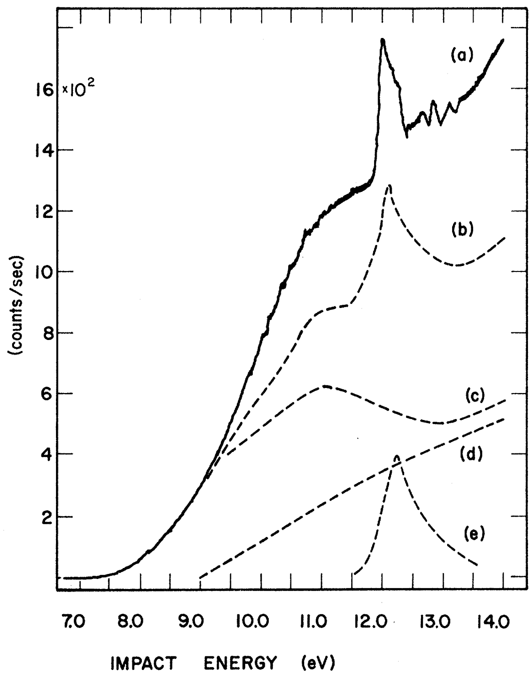

FIG. 1. (a) Metastable excitation function observed in the present work with a resolution of 0.08 eV compared with (b) that observed at lower resolution (Ref. 1) and its constituents (c) $A\,^3\Sigma_u^+$, (d) $a\,^1\Pi_g$, and (e) $E\,^3\Sigma_g^+$. Vertical scale refers to typical detected intensity of (a). Scale of (b)–(e) is arbitrary relative to (a).

smallness of the uv contributions.

The threshold for excitation of $A\,^3\Sigma_u^+$ ($v=0$) is 6.17 eV, but owing to Franck–Condon factors the most favorably excited level is $v=7$ at 7.35 eV, as is evident from the relevant potential curves in Fig. 2. Increased detector efficiency as a function of excitation energy distorts the vibrational contributions to the observed excitation function, and together with Franck–Condon factors this leads to a maximum sensitivity around the $v=12$ threshold near 8 eV. Considerable contribution to $A\,^3\Sigma_u^+$ population arises by cascade after excitation of $B\,^3\Pi_g$ with a threshold of 7.35 eV. The cascade is predominantly to the lower vibrational levels of $A\,^3\Sigma_u^+$, and it therefore contributes little to the observed excitation function because of inefficient detection of the final levels. It should be pointed out, nevertheless, that cascade effects from $B\,^3\Pi_g$ and other triplets dominate the vibrational distribution of population above impact energies of about 10 eV.[1]

The threshold of $a\,^1\Pi_g$ is at 8.55 eV ($v=0$). The principal vibrational states excited[6] are $v=1-5$, with thresholds 8.75–9.52 eV, in agreement with Franck–Condon factors (Fig. 2). No resonant structure is apparent in either the $A\,^3\Sigma_u^+$ or $a\,^1\Pi_g$ channels up to impact energies of 12 eV. In particular, the structures at 11.45 and 11.75 eV, associated with $a\,^2\Sigma_g^+$ resonant state[4] of N_2^-, are absent. In a recent energy-loss experiment[15] on electrons

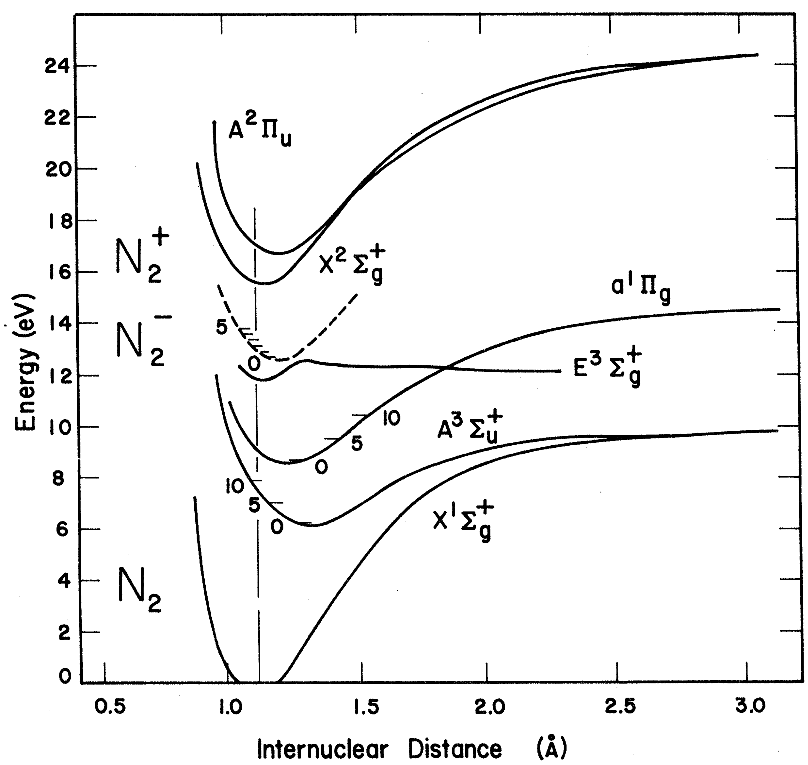

FIG. 2. Internuclear potentials of relevant states of N_2 and N_2^+. Broken-line curve is a possible resonant state of N_2^- observed at impact energies 12–14 eV.

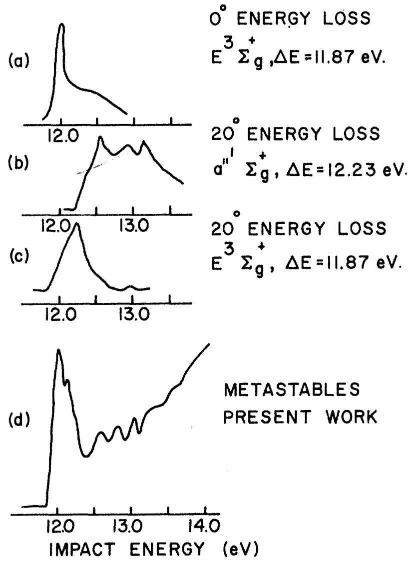

FIG. 3. Details of the energy region 12–14 eV. (a) Electron energy-loss scattering at 0°, $E\ ^3\Sigma_g^+$ channel (Ref. 6); (b) at 20°, $a''\ ^1\Sigma_g^+$ channel (Ref. 7); (c) at 20°, $E\ ^3\Sigma_g^+$ channel (Ref. 7); (d) present work with a resolution of 0.05 eV.

scattered at 90°, these resonances were also not observed in the channels $A\ ^3\Sigma_u^+$ ($v=0, 4$) and $a\ ^1\Pi_g$ ($v=2$). Presumably similar negative results would have been obtained in other vibrational channels.

The steep rise at 11.87 eV is undoubtedly the threshold of the $E\ ^3\Sigma_g^+$ metastable state. The onset agrees with the spectroscopic value of the threshold to well within the 0.03-eV accuracy of our energy calibration. There is obviously a sharp resonance at this threshold which appears to rise to a peak at 12.00 eV. In transmission[5,6] and elastic-scattering[4] experiments a resonance is observed in the region of 11.9 eV, whereas in vibrational excitation[4] of the ground state and energy-loss scattering[6] at 0° into the $E\ ^3\Sigma_g^+$ channel the peak occurs at about 12.0 eV. At 12.02 eV is the position of the $v=2$ level of the above-mentioned $^2\Sigma_g^+$ resonant state of N_2^-.

In Fig. 3 we illustrate details of the region 12–14 eV, where the resolution of our data [curve (d)] was about 0.05 eV. The diagram compares energy-loss scattering at 0° in the $E\ ^3\Sigma_g^+$ channel[6] [curve (a)] and at 20° in the $a''\ ^1\Sigma_g^+$ and $E\ ^3\Sigma_g^+$ channels[7] [curves (b) and (c), respectively]. Our peak immediately above the $E\ ^3\Sigma_g^+$ threshold seems to agree with the 0° data, but is some 0.2 eV below that seen at 20°. In our data a smaller peak was resolved at 12.12 eV, but no structure has been observed in this region in the transmission and energy-loss experiments. It may be a resonance associated with the $v=1$ threshold of $E\ ^3\Sigma_g^+$, which is at 12.14 eV. It has been reported[14] that the $v=1$ level is weakly excited near threshold, and trapped-electron data[8] indicate the intensity to be an order of magnitude less than that for the $v=0$ level. There is also a slight shoulder at 12.25 eV, possibly indicative of a further resonance. This appeared only in our best data and was not reproduced reliably. It has been suggested[5] that structures seen at 11.9 and 12.2 eV in transmission may be due to p-wave resonances appearing very close to the thresholds of their respective parent states $E\ ^3\Sigma_g^+$ and $a''\ ^1\Sigma_g^+$. The over-all width of the entire structure immediately following the $E\ ^3\Sigma_g^+$ threshold in our data was 0.3 eV, somewhat narrower than the 0.4 eV estimated by Borst.[1]

A series of five resonances [Fig. 3(d)] was observed at 12.59, 12.80, 13.03, 13.24, and 13.52 eV presumably occurring in one or both of the $A\ ^3\Sigma_u^+$ and $a\ ^1\Pi_g$ channels. They were not observed in the $E\ ^3\Sigma_g^+$ channel of the energy-loss data, although there is evidence of some structure over the same energy region in the $a''\ ^1\Sigma_g^+$ channel [Fig. 3(b)]. In Table I we compare the energy locations of our resonances with features observed by Sanche and Schulz in a recent transmission experiment.[5] The first two, labeled 5 and 6 by these authors, each lie about 0.06 eV below the first two of our series. The remaining three of our series lie close to the positions of the first three members of band c of the transmission data. The assignment suggested by Sanche and Schulz for these features was a resonant state of N_2^- formed by the temporary attachment of an electron to a Rydberg state of the N_2 molecule. The structure of this state of N_2^- would then be essentially two Rydberg electrons outside an N_2^+ core. The electronic state of the N_2^+ core was suggested by Sanche and Schulz[5] as $A\ ^2\Pi_u$ (see Fig. 2) on the basis of the vibrational spacing of the features observed and their positions relative to another resonance associated with the $X\ ^2\Sigma_g^+$ ground state of the N_2^+ core. In Table I we indicate the estimated accuracy with which we were able to determine the centers of the resonances relative to each other. The accuracy of the last two members

TABLE I. Energy positions and relative intensities of resonances in the energy range 12–14 eV compared with structures observed in transmission.

Metastables (present work) Energy (eV)	Relative intensity	Transmission (Ref. 5) Energy (eV)	
12.59 ± 0.02	0.7	12.64	Structure 5
12.80 ± 0.02	0.8	12.87	Structure 6
13.03 ± 0.02	1.0	13.01	Band c
13.24 ± 0.03	0.6	13.24	
13.52 ± 0.04	0.3	13.47	
		13.70	

was poor, since they were weak and situated on an upward-sloping background. Although in the transmission experiment structures 5 and 6 appeared to belong to different series from band c, our five resonances, to within experimental accuracy, could belong to a single vibrational series, with an average spacing in excellent agreement with the 0.23-eV[5] spacing for the $A\,^2\Pi_u$ state of N_2^+. In Fig. 2 we have sketched as a broken line a possible potential curve for the resonant state of N_2^-. This has been drawn on the assumption that it has the same shape as the N_2^+ grandparent $A\,^2\Pi_u$, and that, as suggested by Sanche and Schulz,[5] the lowest vibrational resonance is at 12.6 eV. The relative intensities (see Table I) of the observed series can be understood in terms of Franck–Condon factors for excitation from the ground $X\,^1\Sigma_g^+$ state of N_2, and the resonances would then autoionize into appropriate vibrational levels of metastable $A\,^3\Sigma_u^+$ and $a\,^1\Pi_g$.

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Semiclassical Collision Theory within the Feynman Path-Integral Formalism*

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A multichannel semiclassical collision theory, based on Feynman's path-integral formulation of quantum mechanics and developed by Pechukas, is discussed. The theory is applied to low-energy, elastic and inelastic, collisions between He^+ and Ne. The calculation involves the solution of a boundary-value problem, and a numerical method for obtaining this solution is presented. The numerical results and the qualitative interpretation of them are compared with the predictions of other available theories.

I. INTRODUCTION

One of the more serious problems encountered in collision theory is that of finding experimental information of sufficient quality and detail to allow one to critically evaluate a particular theoretical interpretation. Not only must the experimental information be quantitatively reproducible, but it should also, ideally, display qualitatively new features. In the area of low-energy atomic scattering this type of information has recently been produced by Lorents and Aberth[1] and has been given an extensive theoretical analysis by Smith and co-workers.[2] The present calculation is an attempt to supplement the existing interpretation of some of this information. We present the results of elastic and inelastic scattering of He^+ off Ne, at an impact energy of 70.9 eV, using a two-state electronic representation, together with a classical nuclear model. The impact energy is sufficiently low so