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OPTICAL IDENTIFICATION OF THE 12.28-eV QUADRUPOLE TRANSITION IN MOLECULAR NITROGEN†

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This Letter reports the optical identification of a predicted ${}^1\Sigma_g^+ - {}^1\Sigma_g^+$ transition in the far-ultraviolet absorption spectrum of molecular nitrogen.

As pointed out by Mulliken¹ the association of a Rydberg $3s\sigma_g$ electron with the ion core $N_2^+ X^2\Sigma_g^+$ must give rise to two Rydberg states, ${}^1\Sigma_g^+$ and ${}^3\Sigma_g^+$. The triplet state is identified as the upper state of the $E^3\Sigma_g^+ - A^3\Sigma_u^+$ emission bands, whereas the singlet state has not been previously observed in the optical spectrum. It can combine with the ground state only through quadrupole or pressure-induced dipole radiation. The transition should be observable in the far-ultraviolet absorption spectrum at sufficiently large pressures and path lengths. Comparison of the related $3s$ -type Rydberg states of N_2 ($E^3\Sigma_g^+$) and CO ($b^3\Sigma^+$, $B^1\Sigma^+$) suggests that the ${}^1\Sigma_g^+$ state of N_2 lies in the range $98\,000$ - $100\,000\text{ cm}^{-1}$. Mulliken has predicted it at $98\,300\text{ cm}^{-1}$. Lefebvre-Brion and Moser² have calculated term values for Rydberg states of N_2 , including the $3s\sigma_g^1\Sigma_g^+$ state, obtaining 12.5 eV ($100\,800\text{ cm}^{-1}$). This predicted state is undoubtedly the one that gives rise to the electron energy-loss peak at 12.26 V , observed by Heideman, Kuyatt, and Chamberlain³ at collision energies of 15.7 and 35 eV , and determined to arise from an electric quadrupole transition by Lassette, Skerbele, and Meyer⁴ through a study of the angular dependence of the inelastic cross section at 500 -

eV collision energy. As illustrated in Fig. 1, the voltage dependence near threshold confirms this identification: The pure quadrupole transitions in N_2 (${}^1\Sigma_g^+ - {}^1\Sigma_g^+$)³ and in He (${}^1S - {}^1S$)⁵ show very closely analogous threshold behavior. This analogy is also evident in the corresponding singlet-triplet excitations (see Fig. 1).

The optical search for this transition thus involves the region ≈ 1009.6 - 1012.9 \AA ($\approx 12.26 \pm 0.02\text{ eV}$). This region has previously been

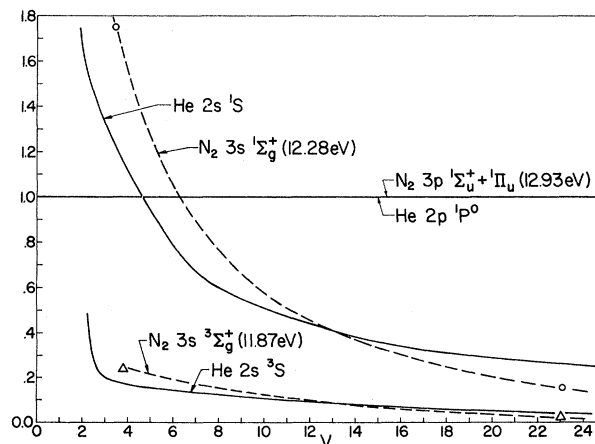


FIG. 1. Strength of quadrupole allowed transitions relative to dipole ones, as a function of energy above threshold, in the electron energy-loss spectra of N_2 [measured at 15.7 - and 35 -eV collision energy (Ref. 3)] and of He ⁵.

investigated by Worley,⁶ who found three faint, red-degraded bands with heads at 1015.37, 1008.52, and 1001.74 Å, denoted by him as the *i* group. These bands originate in the $v'' = 1$ level of the electronic ground state^{7,8} and terminate in the levels $v' = 0$ ("*j*"), 1, and 2 of $b\ ^1\Pi_u$. Since the population of the $v'' = 1$ level at room temperature is 1.1×10^{-5} relative to $v'' = 0$, it should be possible to detect the quadrupole band in the presence of the $b-X$ (1-1) band, which has an oscillator strength⁹ of $\approx 2 \times 10^{-2}$, provided the f value of the quadrupole 0-0 band is no less than $\approx 10^{-7}$.

We have photographed the absorption spectrum of N_2 at pressures up to 40 Torr and 600-cm path length, using a 3-m spectrograph in first and second orders, and a Hopfield continuum light source.¹⁰ The *i*-band heads ($v'' = 1$) were clearly visible at 10 Torr without any real indication of the searched-for quadrupole absorption. However, at 40 Torr, as shown by the densitometer trace of Fig. 2, a broad and symmetric strong absorption feature is clearly superimposed onto the $b-X$ (1-1) band. At 40 Torr the intensity of this new band is much greater than is attributable to the 1-1 band, as evident by comparing in Fig. 2 the relative intensities of the $v'' = 0$ and $v'' = 1$ progressions. Furthermore, the new band extends clearly beyond the head of the 1-1 band at 1008.81 Å. Comparison with the spectrograms of H_2O , O_2 , and CO rule out the presence of these molecules as detectable impurities.

As shown in Fig. 2, the new absorption band is centered around a line at 1009.77 Å, which can be identified as the *Q* branch of the quadrupole band, since this line is too strong for assignment to the 1-1 band. The calculated intensity distribution in the *O* and *S* branches is shown in Fig. 2 [omitting odd-numbered rotational lines; the rotational constant $B_0(N_2^+, X) = 1.92\text{ cm}^{-1}$ was tentatively adopted for the Rydberg $^1\Sigma_g^+$ state]. The observed width of the band as well as the observed steep growth of its intensity with N_2 pressure are best explained by assuming that the rotational lines are pressure broadened and that possibly some of the observed intensity is due to pressure-induced dipole radiation. This Rydberg transition may very well be much more pressure sensitive than the many other forbidden systems of N_2 at longer wavelengths, which are intravalence shell transitions. Diffuseness of lines at similar pressures has recently been found by Ta-

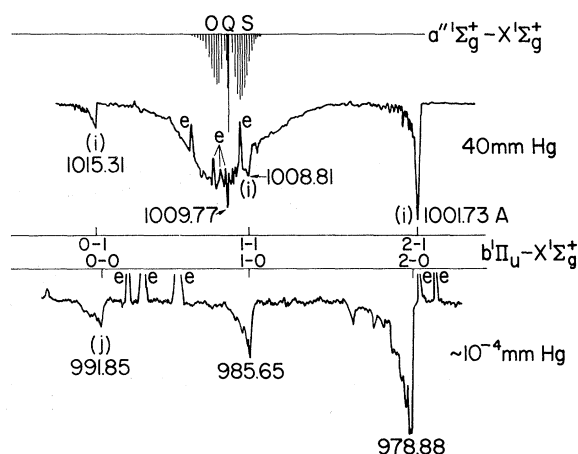


FIG. 2. Microdensitometer tracings of N_2 absorption spectrograms: The strong and wide band observed at 40-mm Hg pressure of N_2 (600-cm path length) is attributed to the $a''\ ^1\Sigma_g^+ - X\ ^1\Sigma_g^+$ quadrupole (or pressure-induced dipole) transition whose theoretical structure and intensity distribution are indicated at the top (for clarity, odd-numbered lines are omitted in all branches). The spectrogram at $\approx 10^{-4}$ mm Hg of N_2 shows the 0-0, 1-0, and 2-0 bands of $b-X$ for comparison of the intensity distribution among these three bands with 0-1, 1-1, and 2-1 bands ("*i*"), showing that the 1-1 transition cannot account for the intensity and width of the band centered near 1009.8 Å. "*e*" denotes emission in the light source.

naka¹¹ in the absorption spectrum of argon in the region 900-1000 Å, i.e., the region which should contain the quadrupole lines $p^5p - p^6$.

The *Q*-branch wavelength of 1009.77 corresponds to a term value of $99\ 032\text{ cm}^{-1}$ (12.278 eV) and agrees well with the electron energy-loss determinations.^{3,4} The optical identification of this transition constitutes the first example of an electronic spectrum of the type $^1\Sigma_g^+ - ^1\Sigma_g^+$. We propose to designate the state ($N_2^+ X, 3s\sigma_g$) $^1\Sigma_g^+$ with the letter *a''* (the state lies above *a* and *a'*, and below *b* and *b'*).

It should be noted that the *a''*-band profile of Fig. 2 is far from representing the profile of the absorption coefficient, since the curve shown is an unreduced tracing of a heavily exposed spectrogram. Further work is in progress to determine oscillator strengths and, through a study of their pressure dependence, to determine the contribution of pressure-induced dipole and of pure quadrupole radiation.

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⁵G. E. Chamberlain, H. G. M. Heideman, J. A. Simpson, and C. E. Kuyatt, in Proceedings of the Fourth International Conference on the Physics of Electronic and Atomic Collisions, Quebec, Canada, 1965 (W. A. Benjamin Inc., New York, 1965).

⁶R. E. Worley, *Phys. Rev.* **64**, 207 (1943).

⁷This identification of the "i" bands has been proposed recently by one of us [K. Dressler, in Proceedings of the International Conference on Spectroscopy,

Bombay, India, 1967 (to be published)], and we are greatly indebted to Professor Worley for sending us a print of his spectrogram to help clarify this question. Our own spectrograms at higher pressures clearly verify the proposed assignment, and Dr. P. K. Carroll (private communication) has independently made the same assignment on the basis of detailed rotational analyses.

⁸Dressler, Ref. 7.

⁹This estimate is based on the f values of the $v''=0$ progression given in G. M. Lawrence, D. L. Mickey, and K. Dressler (to be published) combined with approximate Franck-Condon factors $q(1-0)$ and $q(1-1)$ adopted from R. W. Nicholls, *J. Quant. Spectr. Radiative Transfer* **2**, 433 (1962).

¹⁰Lawrence, Mickey, and Dressler, Ref. 9.

¹¹Y. Tanaka, private communication.

SOME NEW SCHEMES FOR POLARIZING NUCLEI*

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Although nuclei in gases have been polarized using the method of optical pumping introduced by Kastler,¹ no successful experiments have yet been reported for solids. In this note we give details on some new schemes recently proposed² for enhancement of nuclear polarization by optical pumping in solids, abbreviated as ENPOPS. Although there are several cases discussed below, the schemes have these general features: (1) production of an electron spin polarization by pumping with circularly polarized light; (2) transfer of this polarization to nuclear spins through hfs coupling, preferential relaxation processes, or saturation of microwave transitions; (3) transfer of the polarization to abundant nuclei through cross relaxation. In principle, ENPOPS could produce sizable nuclear polarization even at room temperatures, which is an advantage over the present microwave dynamic nuclear polarization methods.³

(A) Contact hfs, high fields.—To consider this case imagine a magnetically dilute crystal at a temperature T containing paramagnetic ions, or perhaps F centers or trapped atoms, in which the electronic ground state is represented by the spin Hamiltonian $\mathcal{H} = g\beta\vec{H} \cdot \vec{J} + A\vec{J} \cdot \vec{I}$, the large first term representing the Zeeman interaction of the ion with an external magnetic field H and the second, the hfs interaction with the nucleus of the ion (or in the case of

F centers, with a near-neighbor nucleus). These energy levels and wave functions (J, J_z, I_z) are shown in Fig. 1 for $J = \frac{1}{2}$ and $I = \frac{1}{2}$, along with an optical level or band to which we induce transitions by illuminating the crystal with circularly polarized light. We assume that by pumping with, say, right-hand polarized light we induce the transition probabilities shown,

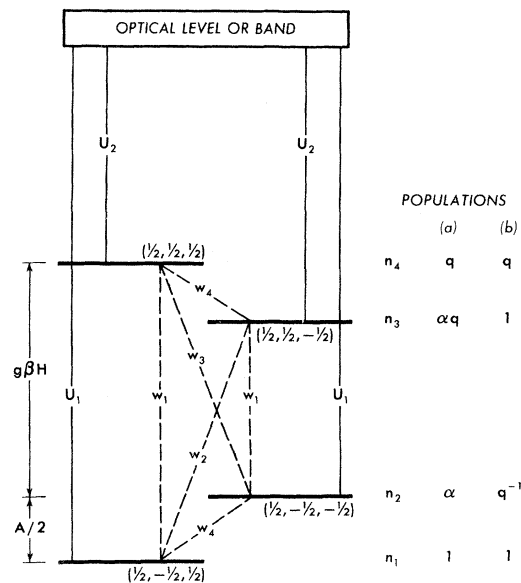


FIG. 1. Levels and transitions for a paramagnetic ion in high field with $S = \frac{1}{2}$ and $I = \frac{1}{2}$. The populations in columns (a) and (b) are obtained by enhancement of the nuclear polarization by optical pumping.