

The singlet–triplet splittings of NCN

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Abstract

The photoelectron spectrum of the cyanonitrene anion, NCN^- , has been measured at 416 and 266 nm. The 266 nm spectrum reveals the $\tilde{a}^1\Delta_g$ and the $\tilde{b}^1\Sigma_g^+$ states together with the $\tilde{X}^3\Sigma_g^-$ ground state for the first time. These low-lying singlet states are separated from the triplet ground state by 1.010 ± 0.010 and 1.629 ± 0.010 eV, respectively. We find a vibrational frequency of 1120 ± 50 cm^{-1} for the ν_1 mode of the $\tilde{b}^1\Sigma_g^+$ state. The ions were produced in a new source particularly suitable for anion precursors with low vapor pressure. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The cyanonitrene radical, NCN, has been proposed as an intermediate in the combustion of hydrocarbons [1] and nitramine [2]. Ultraviolet emission studies [3] have also suggested that NCN is present in the Comet Brorosen–Metcalf. The NCN radical has a $\tilde{X}^3\Sigma_g^-$ ground state with a molecular orbital configuration [4] of $\dots 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 1\pi_g^2$. This configuration also gives rise to two singlet states, the $\tilde{a}^1\Delta_g$ and the $\tilde{b}^1\Sigma_g^+$ states, whose term values with respect to the ground state have been previously unknown. Many studies have been carried out to characterize cyanonitrene theoretically [4–9] and experimentally [1,2,4,10–22]. Optical experiments have been limited to independent studies of the triplet

[11,14,15] and singlet [14] manifolds. Photodissociation experiments involving excitation in both manifolds have recently been carried out in our laboratories [23], but no transitions between the manifolds were observed. By measuring the photoelectron spectrum of the anion, NCN^- , we can access both the triplet and singlet states through detachment of a single electron from the anion $^2\Pi$ ground state. Hence for the first time we are able to obtain the singlet–triplet splittings for the low-lying electronic states of NCN.

Recently, Ellison and co-workers [4] have measured the anion photoelectron spectrum of NCN^- at a photon energy of 3.531 eV. They reported an electron affinity of 2.484 ± 0.006 eV for NCN. At this energy only the transition to the $\tilde{X}^3\Sigma_g^-$ ground state of the neutral is accessible; the $\tilde{a}^1\Delta_g$ state was calculated to lie 1.249 eV above the ground state [4]. In this Letter we report the anion photoelectron spectra of NCN^- taken at photon energies of

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2.977 eV (416 nm) and 4.657 eV (266 nm). At 266 nm, transitions to the $\tilde{a}^1\Delta_g$ and the $\tilde{b}^1\Sigma_g^-$ states are observed and we report their term energies.

2. Experimental

As shown by Ellison, NCN^- is readily produced from cyanamide (H_2NCN). The low vapor pressure of this precursor (estimated to be ~ 4 mTorr at 298 K) necessitated development of a new configuration of our pulsed discharge ion source [24], shown in Fig. 1. The stainless-steel reservoir was filled with cyanamide and placed between a pulsed molecular beam valve and the pulsed discharge assembly. This enables the cyanamide to be entrained in the pulsed molecular beam prior to passing through the discharge. Teflon spacers prevent thermal contact with the pulsed valve and electric discharge plates, allowing the reservoir to be heated without affecting the pulsed valve, although heating was not necessary in this case. Analyses of our photodissociation spectroscopy measurements [23] indicate that this source produces NCN^- ions with vibrational and rotational temperatures of ~ 200 and ~ 50 K, respectively.

The anion photoelectron spectrometer used in this study has been described in detail previously [25,26]. In the work presented here, O_2 at a backing pressure of ~ 3 atm was expanded through the reservoir/pulsed discharge source containing the

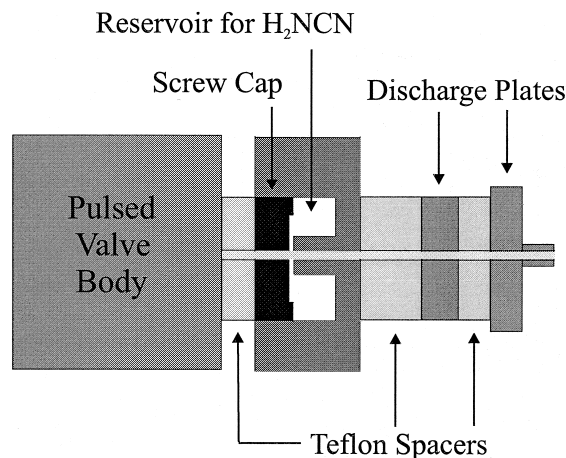


Fig. 1. Schematic of the reservoir/pulsed discharge source. The drawing is not to scale.

precursor cyanamide (H_2NCN). The resultant flow supersonically expands into the source vacuum chamber and passes through a skimmer. The negative ions are extracted perpendicular to their flow direction by a pulsed electric field and injected into a linear reflectron time-of-flight (TOF) mass spectrometer [27,28], affording a mass resolution $m/\Delta m$ of 2000. The ions of interest are selectively photodetached with photons having wavelengths of 266 nm (4.657 eV) and 416 nm (2.977 eV). The photon wavelength of 266 nm was obtained by frequency quadrupling the fundamental of a pulsed Nd:YAG laser. To generate light at 416 nm the Nd:YAG third harmonic at 355 nm was passed through a Raman cell filled with hydrogen at high pressure (325 psig). The electron kinetic energy (eKE) distribution is determined by TOF analysis in a 1 m field-free flight tube. The energy resolution is 8 meV at 0.65 eKE and degrades as $(\text{eKE})^{3/2}$ at higher eKE. All spectra reported were taken at a laser polarization angle $\theta = 90^\circ$, which was found to correspond to the maximum of the photoelectron angular distribution.

3. Results and discussion

Fig. 2 shows the anion photoelectron spectra taken at 266 and 416 nm (see inset). The photoelectron spectra are reported in electron binding energy, eBE, which is defined as $\text{eBE} = h\nu - \text{eKE}$. The inset shows the transition to the $\tilde{X}^3\Sigma_g^-$ ground state of the neutral, a single feature labeled as peak X. This peak is located at $\text{eKE} = 0.496$ eV, affording an electron affinity of 2.481 ± 0.008 eV, in excellent agreement with the value reported by Ellison and co-workers [4]. The structure extending to higher eKE as part of peak X indicates that the $^2\Pi$ anion electronic ground state is internally excited. This is at least partly due to detachment from the two spin-orbit levels of the anion, which are split by only 77 cm^{-1} .

The main spectrum in Fig. 2 shows the 266 nm spectrum with peaks labeled X, A, B, and B1. Peak X is the ground state as previously discussed. Peaks A and B are representing transitions to two excited electronic states. From Hund's rules and the state ordering of the isoelectronic species CCO [29], CNN [30], N_3^+ [31], and NCO^+ [32], these peaks are assigned to the $\tilde{a}^1\Delta_g$ and the $\tilde{b}^1\Sigma_g^-$ states located at

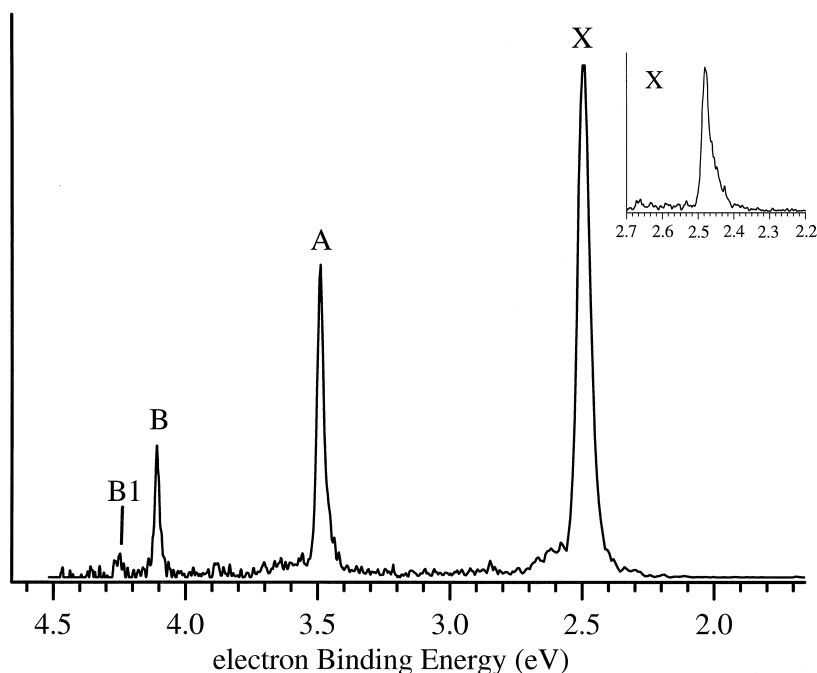


Fig. 2. Photoelectron spectrum of NCN^- taken at 266 and 416 nm (see inset). Both spectra were taken at a laser polarization angle of $\theta = 90^\circ$ with respect to the direction of electron detection.

1.010 ± 0.010 and 1.629 ± 0.010 eV above the ground state, respectively. These spacings are referenced to the peak centers; no attempt was made to fit the peak shapes. Peak B1 is $1120 \pm 50 \text{ cm}^{-1}$ from peak B and we assign this transition to the $\nu_1 = 1$ level of the $\tilde{b}^1\Sigma_g^+$ state, in accord with the known ν_1 fundamentals of the other electronic states [2,14,16]. Like the ground state, these electronic transitions are nearly vertical, and the peaks exhibit the same asymmetry towards higher electron kinetic energy.

The results obtained here allow a full characterization of the low-lying electronic states of NCN , as shown in Fig. 3. Herzberg and Travis [11] identified the first electronic transition from the ground state as the $\tilde{B}^3\Sigma_u^- \leftarrow \tilde{X}^3\Sigma_g^-$ transition having an energy of 4.154 eV. Kroto and co-workers [14] observed another transition within the triplet manifold, the $\tilde{A}^3\Pi_u \leftarrow \tilde{X}^3\Sigma_g^-$ band, with an energy of 3.767 eV. They also observed two transitions within the singlet manifold assigned as the $\tilde{c}^1\Delta_g \leftarrow \tilde{a}^1\Delta_g$ and $\tilde{d}^1\Delta_u \leftarrow \tilde{a}^1\Delta_g$ transitions with energies of 3.725 and 4.385 eV, respectively. With our measurement of the $\tilde{a}^1\Delta_g$ and the $\tilde{b}^1\Sigma_g^+$ term energies we can now properly

reference the excited singlet electronic states to the ground state, as shown in Fig. 3.

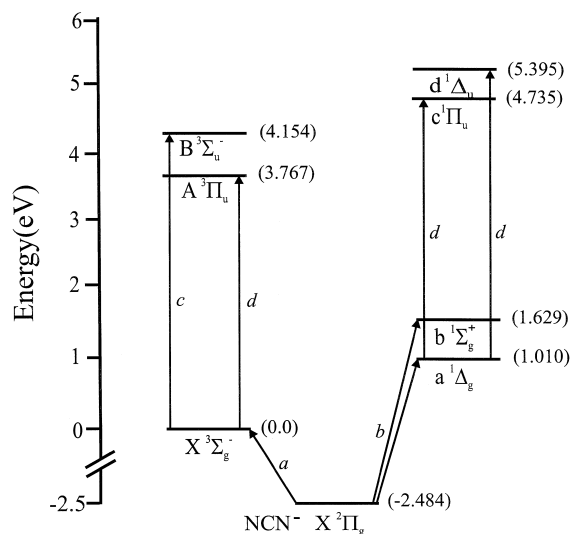


Fig. 3. Energy level diagram of the singlet and triplet manifolds of NCN . Labeled transitions are from the following papers: (a) Ref. [4]; (b) this Letter; (c) Ref. [11]; and (d) Ref. [14].

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References

- [1] K.R. Jennings, J.W. Linnett, *Trans. Faraday Soc.* 56 (1960) 1737.
- [2] G.P. Smith, R.A. Copeland, D.R. Crosley, *J. Chem. Phys.* 91 (1989) 1987.
- [3] C.R. O'Dell, C.O. Miller, A.L. Cochran, W.D. Cochran, C.B. Opal, E.S. Barker, *Astrophys. J.* 368 (1991) 616.
- [4] Clifford, P.G. Wenthold, W.C. Lineberger, G.A. Petersson, G.B. Ellison, *J. Phys. Chem. A* 101 (1997) 4338.
- [5] G. Berthier, L. Kurdi, C.R. Acad. Sci., Paris, Sér. II (Méc., Phys., Chim., Sci. Univers, Sci. Terre) 299 (1984) 1171.
- [6] H.U. Suter, M.B. Huang, B. Engels, *J. Chem. Phys.* 101 (1994) 7686.
- [7] C. Thomson, *J. Chem. Phys.* 58 (1973) 841.
- [8] G.R. Williams, *Chem. Phys. Lett.* 25 (1974) 602.
- [9] J.M.L. Martin, P.R. Taylor, J.P. Francois, R. Gijbels, *Chem. Phys. Lett.* 226 (1994) 475.
- [10] G.P. Smith, R.A. Copeland, D.R. Crosley, *Am. Inst. Phys. Conf. Proc.* (1988) 659.
- [11] G. Herzberg, D.N. Travis, *Can. J. Phys.* 42 (1964) 1658.
- [12] H.W. Kroto, *J. Chem. Phys.* 44 (1966) 831.
- [13] H.W. Kroto, *Can. J. Phys.* 45 (1967) 1439.
- [14] H.W. Kroto, T.F. Morgan, H.H. Sheena, *Trans. Faraday Soc.* 66 (1970) 2237.
- [15] D.E. Milligan, M.E. Jacox, A.M. Bass, *J. Chem. Phys.* 43 (1965) 3149.
- [16] D.E. Milligan, M.E. Jacox, *J. Chem. Phys.* 45 (1966) 1387.
- [17] S.A. Beaten, Y. Ito, J.M. Brown, *J. Mol. Spectrosc.* 178 (1996) 99.
- [18] S.A. Beaton, J.M. Brown, *J. Mol. Spectrosc.* 183 (1997) 347.
- [19] K.D. Hensel, J.M. Brown, *J. Mol. Spectrosc.* 180 (1996) 170.
- [20] M. Wienkoop, W. Urban, J.M. Brown, *J. Mol. Spectrosc.* 185 (1997) 185.
- [21] J.M. Fluornoy, L.Y. Nelson, *Chem. Phys. Lett.* 6 (1970) 521.
- [22] D. McNaughton, G.F. Metha, R. Tay, *Chem. Phys.* 198 (1995) 107.
- [23] R.T. Bise, H.S. Choi, T.R. Taylor, A. Hoops, D.M. Neumark (in preparation).
- [24] D.L. Osborn, D.J. Leahy, D.R. Cyr, D.M. Neumark, *J. Chem. Phys.* 104 (1996) 5026.
- [25] C. Xu, G.R. Burton, T.R. Taylor, D.M. Neumark, *J. Chem. Phys.* 107 (1997) 3428.
- [26] R.B. Metz, A. Weaver, S.E. Bradforth, T.N. Kitsopoulos, D.M. Neumark, *J. Phys. Chem.* 94 (1990) 1377.
- [27] B.A. Mamyrin, D.V. Shmikk, *Sov. Phys. JETP* 49 (1979) 762.
- [28] G. Markovich, R. Giniger, M. Levin, O. Cheshnovsky, *J. Chem. Phys.* 95 (1991) 9416.
- [29] V. Zengin, B.J. Persson, K.M. Strong, R.E. Continetti, *J. Chem. Phys.* 105 (1996) 9740.
- [30] E.P. Clifford, P.G. Wenthold, W.C. Lineberger, G.A. Petersson, K.M. Broadus, S.R. Kass, S. Kato, C.H. DePuy, V.M. Bierbaum, G.B. Ellison, *J. Phys. Chem. A* 102 (1998) 7100.
- [31] J.M. Dyke, N.B.H. Jonathan, A.E. Lewis, A. Morris, *Mol. Phys.* 47 (1982) 1231.
- [32] J.M. Dyke, N. Jonathan, A.E. Lewis, J.D. Mills, A. Morris, *Mol. Phys.* 50 (1983) 77.