

## Infrared Laser Spectroscopy of the Linear C<sub>13</sub> Carbon Cluster



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distilled water vapor from a gas reservoir at 14 torr and room temperature into the microscope until the partial H<sub>2</sub>O pressure rises to  $4 \times 10^{-6}$  torr. We grow films of ice by opening for 10 s a shutter that covers the sample at all times when the ice is not viewed (rate of growth, 18  $\mu\text{m}/\text{hour}$ ). The resulting film is smooth and homogeneous. Bright-field imaging reveals no sign of crystallinity even at high magnification. There is no indication of needle or stalactite-like surface features, and the diffraction pattern directly after deposition does not show crystalline diffraction peaks for deposition temperatures below about 120 K. The form transitions are observed to occur simultaneously across the entire substrate. Low-electron dose imaging techniques minimize sample degradation during viewing. Electron beam damage does not change the diffraction patterns on time scales of each measurement, and we move to a different part of the ice layer in subsequent measurements.

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19. Our choice of nomenclature for the amorphous forms is given by the success of describing amorphous forms by random network models and follows previous suggestions to name the amorphous form I<sub>v</sub> [J. Dubochet, J. Chang, R. Freeman, J. Lepault, A. W. McDowell, *Ultramicroscopy* **10**, 55 (1982)], I<sub>as</sub> (21), or I<sub>a</sub> (17). We prefer this notation to that used in studies related to liquid water, that is, H<sub>2</sub>O(as), H<sub>2</sub>O(as,l), or (H<sub>2</sub>O)<sub>as</sub>. Although the Roman numeral polymorph designations are generally applied only to the crystalline phases, the structure of the low-density amorphous form is well represented by a disordered ice I network and the high-density form by such a network including interstitial water. We believe that alternative models for high-density ice based on one of the 11 high-pressure phases of water (4, 12) are unlikely because they are either outside their stability regime or demand a form of proton ordering [B. Kamb, in *Water and Aqueous Solutions*, R. A. Horne, Ed. (Wiley-Interscience, New York, 1973), pp. 9–24]. Of course, we realize that an amorphous form may not have a unique structure. For example, the high-density form might have a varying content of interstitial water if deposition conditions vary. The justification for giving names to these forms is that there are well-defined transition zones between the different forms. Alternative amorphous forms have been made in the laboratory (and similarly bear some relation to ice I) by pressure-induced amorphousing hexagonal ice I<sub>h</sub> at 77 K and 10 kbar [O. Mishima, L. D. Calvert, E. Whalley, *Nature* **310**, 393 (1984)]. This synthetic ice shows a similar high- to low-density transition, but at a higher temperature of 105 to 128 K [Y. P. Handa, O. Mishima, E. Whalley, *J. Chem. Phys.* **84**, 2766 (1986); A. Bizid, L. Bosio, A. Defrain, M. Oumezzine, *ibid.* **87**, 2225 (1987); J. Tse, *ibid.* **96**, 5482 (1992)].
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## Infrared Laser Spectroscopy of the Linear C<sub>13</sub> Carbon Cluster

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The infrared absorption spectrum of a linear, 13-atom carbon cluster (C<sub>13</sub>) has been observed by the use of a supersonic cluster beam–diode laser spectrometer. Seventy-six rovibrational transitions were measured near 1809 wave numbers and assigned to an antisymmetric stretching fundamental in the  $1^1\Sigma_g^+$  ground state of C<sub>13</sub>. This definitive structural characterization of a carbon cluster in the intermediate size range between C<sub>10</sub> and C<sub>20</sub> is in apparent conflict with theoretical calculations, which predict that clusters of this size should exist as planar monocyclic rings.

The structure and bonding in pure carbon molecules have been of interest for many years because of the importance of these species in many contexts, ranging from dust-grain formation in the interstellar medium to soot formation in combustion systems. Recently, this interest in carbon clusters has intensified because of the dramatic emergence of fullerene science, centered primarily about the discovery and characterization of the C<sub>60</sub> molecule and other members of this “third form of carbon.” A review article by Weltner and Van Zee describes research conducted before 1989 (1). Experimental (2) and theoretical (3) evidence suggests that the formation of C<sub>60</sub> and other fullerenes proceeds by a mechanism in which small carbon clusters undergo condensation from linear chains through monocyclic rings and finally to large three-dimensional, cage-like structures. A detailed characterization of this mechanism, as well as those for related processes like soot formation, requires a thorough understanding of how the structure and bonding evolve in smaller carbon clusters as the cluster size increases.

Extensive theoretical and experimental efforts have been under way for several years to elucidate these mechanisms. From theoretical considerations, the picture that has emerged is that the small, odd-numbered clusters of C<sub>3</sub> to C<sub>9</sub> exist exclusively as cumulenic linear chains with  $1^1\Sigma_g^+$  ground electronic states, whereas the even-numbered clusters of C<sub>4</sub>, C<sub>6</sub>, and C<sub>8</sub> have two nearly isoenergetic structural isomers, a  $3^1\Sigma_g^-$  linear chain and a nearly planar singlet cyclic ring (4–6). Above C<sub>9</sub> a transition occurs, and the ground-state structures of both even and odd clusters become planar monocyclic rings, while the corresponding linear structures become relatively high in energy (5, 7, 8). This trend is thought to continue for C<sub>10</sub> to C<sub>20</sub>. As the cluster size increases toward C<sub>20</sub>, high-level ab initio calculations become unfeasible, although several calculations at lower levels of theory have been reported (9, 10). Ion mobility measurements indicate that a rich variety of structures begins to form above C<sub>20</sub>, including planar monocyclic and polycyclic rings (11). Some calculations suggest that clusters as small as C<sub>18</sub> may exist as fullerenes (10), although there is no experimental evidence to support this suggestion. However, it is clear that fullerenes become the most stable structures at sizes larger than C<sub>30</sub>.

Experimental verification of this picture

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is by no means complete. During the last few years, the linear structures of  $C_3$  (12, 13),  $C_4$  (12, 14),  $C_5$  (12, 15),  $C_6$  (16),  $C_7$  (12), and  $C_9$  (17) have been definitively characterized through high-resolution laser spectroscopy. Cyclic isomers, which are predicted to exist for even-numbered carbon clusters in this size range, have so far eluded detection by spectroscopic techniques. Indirect evidence for the existence of nonlinear isomers of small carbon clusters, including the rhombic form of  $C_4$ , has been obtained from coulomb explosion imaging experiments and from measurements of electron photodetachment cross sections (18). Structural data for neutral carbon clusters in the range of  $C_{10}$  to  $C_{20}$  are extremely sparse. The linear triplet form of  $C_{10}$  trapped in an inert gas matrix has been observed with electron spin resonance spectroscopy (19), and indirect evidence for cyclic  $C_{10}$  as well as both the linear and the cyclic forms of  $C_{11}$  has been obtained from anion photoelectron spectroscopy (20).

The only other experimental structural information for carbon clusters in this intermediate size range has been extracted from reactivity (21) and mobility (11, 22) studies of carbon cluster ions. Relative cross sections and product distributions for carbon cluster cation reactions with simple gas-phase molecules (for example,  $O_2$ ,  $H_2O$ , and  $NH_3$ ) have been deduced from mass spectrometry (20). These measurements generally suggest the existence of linear structures for  $C_5^+$  and  $C_6^+$ , both linear and cyclic isomers for  $C_7^+$  to  $C_{10}^+$ , and cyclic structures for cluster ions larger than  $C_{10}^+$ . However, Smalley and co-workers claim evidence for linear chain structures of neutral carbon clusters as large as  $C_{30}$ , on the basis of reaction product distributions (23). Mobility data from gas-phase ion chromatography measurements by Bowers and co-workers (11) provide more extensive structural information and isomer distributions for cluster ions as large as  $C_{84}^+$ . Mobility measurements on carbon cluster cations confirm reactivity measurements that indicate the existence of both linear chains and monocyclic rings for  $C_7^+$  to  $C_{10}^+$  and monocyclic rings for  $C_{11}^+$  to  $C_{20}^+$ . Indeed, the only structures indicated in the intermediate size range between  $C_{11}^+$  and  $C_{20}^+$  were monocyclic rings. In similar mobility measurements on carbon cluster anions, the surprising result that linear structures coexist with monocyclic rings for  $C_{10}^-$  to  $C_{20}^-$  was obtained (22). In fact, under certain conditions the chain structures of  $C_{11}^-$  to  $C_{14}^-$  are most abundant. These latter results are consistent with an earlier photodetachment spectroscopic study that found indirect evidence for linear carbon cluster anions larger than  $C_9^-$  (24) and with a recent Fourier transform mass spectrometry

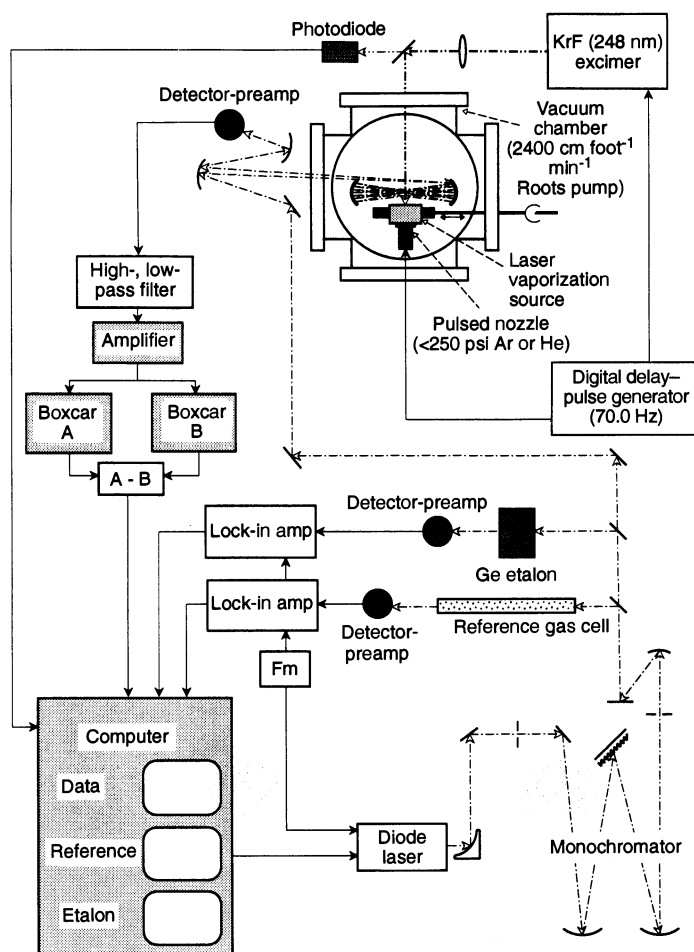
study of anion distributions that concluded that the transition from chains to rings occurs at  $C_{13}^-$  or  $C_{14}^-$  (25). Bowers and co-workers suggest that the existence of linear  $C_{10}^-$  to  $C_{20}^-$  may mean that linear neutral carbon clusters also exist in this size range, because electron attachment to neutral carbon clusters is a possible mechanism for anion formation.

The  $C_{13}$  molecule has been the subject of a recent theoretical investigation. Hutter *et al.* performed density functional theory calculations to determine ground-state geometries and relative stabilities for  $C_2$  to  $C_{18}$  (9). The cyclic isomer of  $C_{13}$  was found to be 20 to 30 kcal/mol more stable than the linear form. The results of these calculations are largely in agreement with early molecular orbital theory calculations (4), as well as modern high-level *ab initio* studies

(5, 7, 8), that predict monocyclic ring structures for carbon clusters larger than  $C_9$ .

We report the measurement and analysis of the rovibrational spectrum of linear  $C_{13}$ , arising from an antisymmetric stretching fundamental in the region near  $1809\text{ cm}^{-1}$ . This definitive structural characterization of a carbon cluster in the intermediate size range between  $C_{10}$  and  $C_{20}$  provides direct evidence for the existence of low-energy linear isomers for neutral carbon clusters larger than  $C_{11}$ . The rovibrational band of  $C_{13}$  reported here was obtained with the Berkeley supersonic cluster beam–diode laser spectroscopy apparatus (12, 16, 17) (Fig. 1). Three infrared (IR) absorption bands at 1804, 1818, and  $1844\text{ cm}^{-1}$  observed from carbon clusters trapped in a rare-gas matrix have been tentatively assigned to cyclic  $C_{10}$  and  $C_{11}$  by Martin *et al.* on the basis of ab

**Fig. 1.** The Berkeley supersonic cluster beam–diode laser spectrometer. A pulsed supersonic molecular beam of carbon clusters is produced by the 248-nm excimer laser [Questek (Acton, Massachusetts) v $\beta$ ] ablation of a high-density graphite rod (POCO Graphite, Decatur, Texas), which rotates and translates in the throat of a 1 mm by 15-mm slit nozzle. A 1000- to 2000-kPa pulse of He is delivered by a Series 9 General Valve operated by an IOTA 1 Pulse Driver (General Valve, Fairfield, New Jersey) that sweeps the carbon vapor through the nozzle and into a vacuum chamber maintained at a pressure of 100 mtorr by a 1000  $s^{-1}$  roots blower backed by two dual-stage mechanical pumps (Edwards, Sussex, United Kingdom). The molecular beam is intersected 10 mm downstream from the nozzle by 18 to 24 passes of a focused IR diode laser beam that is produced by a 1790- to  $1900\text{-cm}^{-1}$   $Pb_{1-x}Se_x$  diode (Mütek, Herrsching, Germany) operated by a Laser Analytics (Bedford, Massachusetts) spectrometer (Fm, frequency modulator). Transient absorption signals are measured with a HgCdTe photoconductive detector (SBRC) and gated boxcar integration (SRS, Sunnyvale, California), and the data are collected by a PC 486-DX computer that steps the diode laser in 20-MHz frequency intervals after averaging 30 to 100 points. The averaged time profile of the detector output is observed with a Tektronix TDS 320 digital oscilloscope that enables precise adjustment of the boxcar gates. The timing sequence of the experiment is controlled with an SRS DG535 pulse generator. Frequency calibration of the data is accomplished by referencing the lines to the fringe spectrum of a vacuum-spaced  $285.3(8)\text{-MHz}$  (at  $1800\text{ cm}^{-1}$ ) free spectral-range etalon (Laser Analytics) and three rovibrational transitions of  $H_2O$  in the region between 1808 and  $1810\text{ cm}^{-1}$  (28).



initio calculations at the Hartree-Fock level (8). However, the only absorption signals that we have measured in this spectral region are those reported here. Seventy-six rovibrational transitions were detected in the frequency region between 1808.1 and 1809.7  $\text{cm}^{-1}$ , all of which have been assigned to an antisymmetric stretching vibration of linear  $\text{C}_{13}$  with values of the rotational quantum number,  $J$ , of up to 80 in the P branch and 74 in the R branch (Fig. 2). The observed spectrum is characteristic of a linear centrosymmetric molecule with nuclear spin weights of zero for antisymmetric rotational energy levels, in that every other rovibrational transition is missing from the spectrum. The assignment of the spectrum was complicated by the fact that three of the lowest  $J$  transitions near the band origin were not detected, which allows for more than one possible rotational assignment. The assignment presented here was selected because the lowest  $J$  P- and R-branch lines have nearly the same relative intensity. Therefore, these transitions are assumed to arise from the same rotational energy level. This condition is satisfied only if these lowest  $J$  lines are assigned as P(4) and R(4) (Fig. 2). The rest of the spectrum is assigned accordingly. In any case, all possible rotational assignments yield similar rotational constants. The relative intensities of all transitions in this band can be reproduced approximately by assuming a rotational temperature of 10 K.

Observed frequencies and ground- and upper-state combination differences were analyzed by a least-squares fit. The molec-

ular parameters obtained from this fit are presented in the caption to Fig. 2. An excellent fit ( $\text{SD} = 4.5 \times 10^{-4} \text{ cm}^{-1}$ ) was obtained without the inclusion of distortion constants; therefore, only lower- and upper-state rotational constants are given. Centrifugal distortion parameters are statistically determinable from the data, and the inclusion of these constants improves the quality of the fit somewhat. However, distortion parameters obtained in this way are anomalous both in magnitude and in sign in the fit to both observed frequencies and combination differences, and no physical significance can be assigned to them. A similar effect was observed for  $\text{C}_7$  and  $\text{C}_9$ , for which large, negative distortion constants were taken as evidence for slight perturbations to the energy levels (12, 17). The inclusion of distortion constants in the fit to the present data set does not substantially alter the magnitude of the rotational constants, so they were not included in the final fit. In the fit to observed frequencies, the upper- and lower-state rotational constants were found to be highly correlated. This correlation was removed by fitting the combination differences,  $R(J) - P(J)$  for upper-state levels and  $R(J) - P(J+2)$  for lower-state levels. The rotational constants obtained in this way were identical to those calculated from the direct fit to observed transitions.

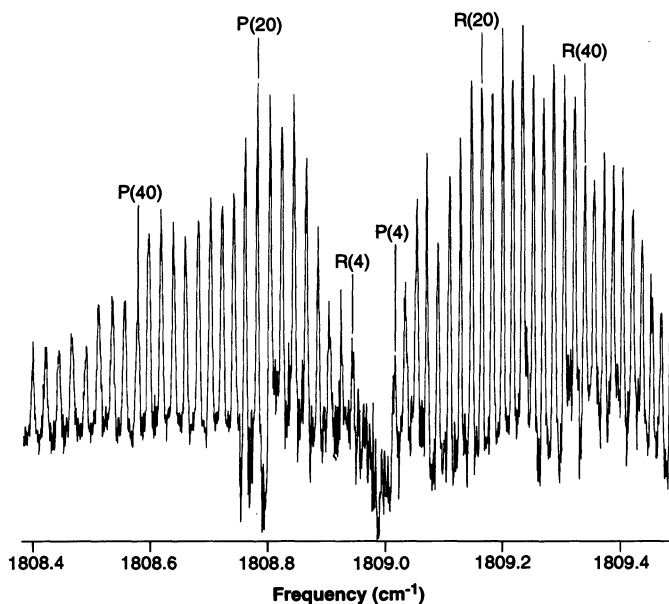
These rovibrational transitions have been assigned to the linear  $\text{C}_{13}$  carbon cluster on the basis of the following criteria: The introduction of impurities containing  $\text{N}_2$ ,  $\text{O}_2$ , and water vapor into the He carrier

gas caused a substantial decrease in the intensity of the transitions. This observation provides evidence that the absorber is a pure carbon cluster rather than a long-chain hydrogen-, oxygen-, or nitrogen-containing carbon molecule. Assignment of these transitions to a pure carbon cluster is also consistent with the observed nuclear spin statistics and with findings from our earlier experiments. Additionally, precise values for the rotational constants of linear  $\text{C}_3$  to  $\text{C}_7$  and  $\text{C}_9$  have been measured (12, 14, 16, 17), from which it is possible to calculate average carbon-carbon double bond lengths for each cluster. These average bond lengths range from 1.27 to 1.30 Å and are in excellent agreement with theoretical predictions for the bond lengths of cumulenic structures (5–7). The average bond lengths for larger linear carbon clusters should be close to this range. Linear  $\text{C}_{13}$  is the only carbon cluster for which an average carbon-carbon bond length within the above range reproduces the measured rotational constant. The  $\text{C}_{13}^-$  anion has been ruled out as a carrier of these transitions because, if the molecular orbitals of larger linear clusters follow the same trends as  $\text{C}_3$  through  $\text{C}_9$ ,  $\text{C}_{13}^-$  should have a  $^2\Pi$  ground electronic state, in which case both even- and odd-numbered transitions would be observed in the spectrum. Furthermore, we strongly suspect that neutral species greatly outnumber ions in the molecular beam.

A cumulenic bonding configuration (all double bonds) with a  $^1\Sigma_g^+$  electronic state has been assumed in the assignment of these transitions, analogous to the odd-numbered  $\text{C}_3$  through  $\text{C}_9$  clusters. The fact that every other transition is missing from the spectrum confirms that the molecule is in a  $\Sigma$  state, and the lack of strong evidence for fine-structure splittings due to electron spin interactions is consistent with a singlet electronic state. In addition, the observed similarity in the relative intensities of the lowest  $J$  P- and R-branch lines [labeled P(4) and R(4) in Fig. 2], as discussed above, suggests that these transitions arise from the same, even-numbered rotational-energy level. The assignment of odd numbers to the transitions would require these two lines to arise from different rotational-energy levels. Therefore, a symmetric electronic state is assumed.

It is not certain whether these  $\text{C}_{13}$  data can be assigned to a known matrix IR absorption band. The best candidate is a matrix absorption at 1804  $\text{cm}^{-1}$ . However, in previous measurements of smaller linear carbon clusters, the matrix environment induced a red shift of the band origin that increased systematically as the cluster size increased (12). For  $\text{C}_9$ , the band origin observed in the matrix was red-shifted by

**Fig. 2.** A part of the rovibrational spectrum of an antisymmetric ( $\sigma_u$ ) stretch fundamental of linear  $\text{C}_{13}$ . Seventy-six rovibrational transitions were measured in the 1808.1- to 1809.7- $\text{cm}^{-1}$  region and assigned to  $J$  values as high as 80. Analysis of these transitions yielded a band origin of 1808.96399(7)  $\text{cm}^{-1}$  and rotational constants of 0.0047324(6)  $\text{cm}^{-1}$  for the ground state and 0.0047218(6)  $\text{cm}^{-1}$  for the upper state (values in parentheses are uncertainties in the last digit). The standard deviation of the nonlinear least squares fit to the measured peak positions was  $4.5 \times 10^{-4} \text{ cm}^{-1}$ . An average carbon-carbon bond length of 1.2770(5) Å was obtained from the rotational constant. Relative intensities for these transitions can be reproduced by assuming a Boltzmann distribution and a rotational temperature of 10 K. The fact that only even  $J$  states were observed, as well as the absence of other features in this region, confirms that the carrier is a centrosymmetric linear molecule.



more than  $15 \text{ cm}^{-1}$  compared to the gas-phase value (17). Thus, the observed matrix band of  $\text{C}_{13}$  should be in a frequency region between  $1780$  and  $1795 \text{ cm}^{-1}$ .

From the data observed so far, it appears for neutral and anionic carbon clusters from  $\text{C}_{10}$  to  $\text{C}_{20}$  that linear and cyclic isomers coexist in laser-vaporized graphite, despite theoretical predictions that the cyclic rings should be considerably more stable [ $\geq 20$  kcal/mol (7–9)] than the linear chains. At the high temperature (approximately 4000 K) of graphite vaporization, entropy strongly favors the formation of linear over cyclic isomers because of the higher density of states that results from the low bending frequencies of the linear structures. Therefore, it may be that the cyclic structures must be vastly more stable than the linear structures to be observed under these conditions. Furthermore, in the molecular beam source used for this experiment, the graphite vapor is rapidly cooled by supersonic expansion, which may result in the "freezing-out" of high-energy structures produced in the initial vaporization. Recently, von Helden and colleagues reported an experimental (26) and theoretical (27) study of  $\text{C}_7^+$  that illustrates these points. Both linear and cyclic isomers of  $\text{C}_7^+$  were observed in mobility measurements. Ab initio calculations revealed that the cyclic structure should be approximately 20 kcal/mol more stable than the linear structure. A barrier to isomerization was also calculated to be about 50 kcal/mol. Thus, despite the large energy separation between the two isomers, a substantial number of linear structures form because of entropy and are subsequently frozen out because of the large barrier to isomerization. On the basis of these considerations, it seems likely that large linear carbon clusters play a major role in the chemistry of high-temperature, carbon-rich environments, despite the greater stability of the cyclic isomers.

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## Direct Spectroscopic Detection of a Zwitterionic Excited State

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Two electrons in two weakly coupled orbitals give rise to two states (diradical) with electrons residing in separate orbitals and two states (zwitterionic) with both electrons paired in one orbital or the other. This two-electron, two-orbital state manifold has eluded experimental confirmation because the zwitterionic states have been difficult to locate. Two-photon excitation of fluorescence from  $\text{Mo}_2\text{Cl}_4(\text{PMe}_3)_4$  ( $D_{2d}$ ) has been measured with linearly and circularly polarized light. From the polarization ratio and the energy of the observed transition, the  $2^1A_1$  ( $\delta^*\delta^*$ ) excited state has been located and characterized. In conjunction with the one-photon allowed  $1B_2$  ( $\delta\delta^*$ ) excited state, the zwitterionic state manifold for the quadruply bonded metal-metal class of compounds is thus established.

Two electrons in weakly coupled orbitals on two centers give rise to four states: two low-energy "diradical" states arising from one electron in each orbital with spins opposed (singlet) and parallel (triplet), respectively, and two higher energy "zwitterionic" singlet states derived from the anti-symmetric and symmetric linear combinations, respectively, in which both electrons are paired in one orbital of either center. In this model, the singlet and triplet diradical

states are energetically far removed from the ionic states, and the energy gaps within the diradical and zwitterionic states are small and equal. When the two orbitals are uncoupled, the diradical states are degenerate, as are the zwitterionic states. This two-electron, two-orbital manifold of states holds a central place in bonding descriptions. After their espial in the valence bond theory of Heitler and London (1), these states were invoked by Mulliken to describe ethylene upon twisting (2) and dihydrogen at long internuclear distances (stretched hydrogen) (3). They were subsequently recognized in Coulson and Fischer's treatment of dehydrogen by molecular orbital theory

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