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AB INITIO STUDY OF THE ELECTRIC DIPOLE
TRANSITION MOMENT FOR THE ELECTRONIC $\tilde{C} \leftarrow \tilde{X}$
TRANSITION IN ACETYLENE: THEORETICAL PREDICTIONS
OF THE ABSORPTION AND MAGNETIC
CIRCULAR DICHROISM INTENSITIES

JAMES O. JENSEN
GEORGE F. ADAMS
CARY F. CHABALOWSKI

DECEMBER 1990

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13. ABSTRACT (Maximum 200 words) The electric dipole transition moment has been calculated <i>a priori</i> for the $\tilde{C}(1^1\Pi_u) \leftarrow \tilde{X}(1^1\Sigma_g^+)$ electronic transition as a function of R(C-C), using <i>ab initio</i> quantum chemical techniques including state averaged, complete active space MCSCF and multireference CI. The transition moment is then averaged over the vibrational wavefunctions for the C-C stretch, and theoretical predictions are made for the absorption oscillator strength and the magnetic circular dichroism (MCD) intensities, $\langle \Delta \epsilon \rangle_1$, for the lowest four vibrational bands originating from $v=0$ in X. This study predicts an oscillator strength for absorption of $f=0.157$ (summed over $v'=0-3$), to be compared to an early experimental value of 0.062 ± 0.0092 . And for the MCD 0-0 band, the calculations predict $\langle \Delta \epsilon \rangle_1 = 0.0179$ while the experimental value is reported to be 0.0125 ± 0.001 (cgs units).				
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1. INTRODUCTION

In this first of two papers we report the *a priori* calculation of the electric dipole transition moment as a function of the C-C bondlength for the $\tilde{C}^{\leftarrow}\tilde{X}$ electronic transition in acetylene. This moment is then used to predict the oscillator strength for absorption and the electronic magnetic circular dichroism (MCD) spectra using a newly implemented code. The $\tilde{C}^{\leftarrow}\tilde{X}$ electronic transition occurs in the 153-140 nm region, with the $\nu_2(0-0)$ (C-C symmetric stretch) at 151.8 nm (65860 cm^{-1}) (Price 1935; Wilkinson 1958; Nakayama and Watanabe 1964; Moe and Duncan 1952; Gadanken and Schnepf 1976). Previous experiments (Price 1935; Wilkinson 1958; Nakayama and Watanabe 1964; Moe and Duncan 1952), as well as *ab initio* calculations (Peric, Buenker, and Peyerimhoff 1984; Kammer 1974; Demoulin and Jungen 1974; Demoulin 1975), have assigned the $\tilde{C}$ state to the linear Rydberg $1^1\Pi_u$ state.

Demoulin and Jungen (1974) used an *ab initio* quantum chemical approach, but only at the SCF level, to predict an absorption oscillator strength of 0.072 for the (vertical) $\tilde{C}^{\leftarrow}\tilde{X}$ transition. An early experimental estimate of the oscillator strength was reported by Moe and Duncan (1952) to be 0.062, while a more recent study by Gedanken and Schnepf (1976) reports both the MCD and absorption spectra. Unfortunately, in the absorption spectrum, the well separated band maxima appear to reside upon a very broad band of non-negligible intensity. No attempt was made to reveal the source of this broad band; however, an attempt was made to subtract out the intensity of this underlying band from that which was assumed to belong only to the $\tilde{C}^{\leftarrow}\tilde{X}$ transition. After having done this, they report the values for the square of the electric transition dipole moments for the first four vibrational bands. From this, one can readily obtain the oscillator strengths for absorption which sum to 0.110 for these four vibrational bands.

The MCD spectrum shows a well resolved vibrational structure corresponding to ν_2 , with a dispersive band shape indicative of a degenerate $\tilde{C}$ state. In contrast to the absorption spectrum, the MCD shows no obvious signs of overlapping with the broad band seen in absorption. If one then extracts the electric transition dipole moment from the MCD intensities (based on a magnetic dipole moment of 0.5), one gets the value of 0.11 for the sum over the four vibrational bands, which agrees well with the value extracted from their "corrected" absorption intensities. Thus, the estimates of the oscillator strength vary over a wide range from 0.062 to 0.11, suggesting the need for an estimate of this transition intensity based upon high quality *ab initio* calculations.

A transition from a non-degenerate ground state to a degenerate excited state, as in the case in the $\tilde{C} \leftarrow \tilde{X}$ transition, should have a large contribution to the MCD from the $\mathcal{A}$ -term (Stephens 1976; Piepho and Schatz 1985). In this study, it is assumed that the entire MCD intensity can be described by this $\mathcal{A}$ -term, which is calculated via *ab initio* quantum chemical methods. The wavefunctions will be generated using a large atomic gaussian basis set and state-averaged MCSCF plus configuration interaction (CI). In the second paper, we will extend the calculations (both oscillator strengths and MCD intensities) to the 190-170 nm spectral region which includes the $\tilde{B} \leftarrow \tilde{X}$ transition. An excellent review of the literature pertaining to the $\tilde{C} \leftarrow \tilde{X}$ transition (as well as other singlet states) can be found in the paper by Peric, Buenker, and Peyerimhoff (1984).

2. METHODS

2.1 Quantum Chemical Approach. The CI method used to obtain the zeroth-order wavefunctions is the symbolic matrix element, direct-CI method of Liu and Yoshimine (1981). The molecular orbitals (MO) used as a basis set for the CI expansions were obtained from a state-averaged, multi-configuration self-consistent field complete active space (SA-MCSCF) approach (Diffenderfer and Yarkony 1982). The nonactive MOs from the SA-CASSCF were rotated to be eigenfunctions of the closed shell Fock operator corresponding to the state-averaged density. The active molecular orbitals are taken as the natural orbitals determined from the MCSCF. The SA-CASSCF procedure is the general second-order, density matrix-driven MCSCF algorithm of Lengsfeld (1980). From the SA-CASSCF procedure, one obtains a set of molecular orbitals determined by minimizing the energy functional

$$E_{\text{avg}} = \sum_k w_k \langle \Psi_k^o | H^o | \Psi_k^o \rangle = \sum_k w_k E_k \quad (1)$$

where the Ψ_k^o 's are the eigenfunctions of the H^o , the non-relativistic Hamiltonian operator, in the space of the CASSCF expansion

$$\Psi_k^o = \sum_i c_i^k \psi_i. \quad (2)$$

Above, the w_k s are the nonnegative weighting factors for the electronic states which do not vary as a function of internuclear separation, and the ψ_i configuration state functions (CSF) composed of the MOs determined in the SA-CASSCF. The weights were chosen to provide a balanced description of the states of interest.

2.2 Spectral Intensities. The oscillator strength for the electronic transition from the ground state $\tilde{X}(1^1\Sigma_g^+)$ to the excited state $\tilde{C}(1^1\Pi_u)$ is given by

$$f = \frac{2}{3} \Delta E |\langle \tilde{X} | \vec{m} | \tilde{C} \rangle|^2 \quad (3)$$

with the transition energy, ΔE , given in au's. In the reduced spacial symmetry of D_{2h} , this becomes

$$f = \frac{2}{3} \Delta E \left\{ |\langle \tilde{X}(A_g) | \vec{m} | \tilde{C}(\Pi_u) \rangle|^2 + |\langle \tilde{X}(A_g) | \vec{m} | \tilde{C}(\Pi_g) \rangle|^2 \right\}. \quad (4)$$

The MCD intensity for a transition involving a non-degenerate ground state, $\tilde{X}$, and a possibly degenerate excited state, $\tilde{I}$, is given by the difference between the decadic molar extinction coefficients for left and right circularly polarized light, i.e., $\Delta \epsilon = \epsilon_L - \epsilon_R$ (Stephens 1976; Piepho and Schatz 1983)

$$\frac{\Delta \epsilon}{E} = 653.2 \mu_B \left[\overline{A_1} \left(\frac{\partial f}{\partial E} \right) \right] \cdot H \quad (5)$$

where E is energy, f a lineshape function, H the magnetic field, and $\overline{A_1}$ is given by

$$\overline{A_1} = \frac{Im}{3} \sum_{\lambda, \lambda'} \left[\langle \tilde{I}_\lambda | \vec{\mu} | \tilde{I}_{\lambda'} \rangle \cdot \langle \tilde{X} | \vec{m} | \tilde{I}_\lambda \rangle + \langle \tilde{X} | \vec{m} | \tilde{I}_{\lambda'} \rangle \cdot \langle \tilde{I}_\lambda | \vec{\mu} | \tilde{X} \rangle \right] \quad (6)$$

with $\vec{\mu}$ and $\vec{m}$ being the magnetic and electric dipole moment operators, μ_B the Bohr magneton ($4.669 \times 10^{-4} \text{ cm}^{-1}/\text{Gauss}$), and λ specifies the degenerate components of $\tilde{I}$. Equation 6 takes into account the fact that the molecules are randomly oriented. The units are cgs with energies in cm^{-1} , electric dipole moments in Debye, and the magnetic field in Gauss. The operator, $\vec{m}$, is chosen in the length form. The symbols for the electric and magnetic dipole moment operators were chosen to be consistent with the literature on MCD published by Stephens (1976) and co-workers.

From Equation 6, one sees that the $\overline{A_1}$ term is derived for a truly degenerate, excited state, $\tilde{I}$, and that a MCD band attributed to such a state will exhibit a characteristic derivative lineshape. The band shape is often used to determine if a transition involves a degenerate excited state. The reader is referred to Stephens (1976) and Piepho and Schatz (1983) for detailed discussions of MCD theory, applications, and band shapes.

As noted earlier, the $\tilde{C}\leftarrow\tilde{X}$ band system shows an essentially pure derivative band shape consistent with a linear, degenerate Π_u upper electronic state. Based on the assumption that the intensity of the MCD band comes strictly from the $\overline{A}_1$ term, we get (in D_{2h} symmetry)

$$\overline{A}_1' = \frac{2Im}{3} \left[\langle \tilde{C}(\Pi_{ux}) | \mu_z | \tilde{C}(\Pi_{uy}) \rangle \langle \tilde{X}(A_g) | m_x | \tilde{C}(\Pi_{ux}) \rangle \langle \tilde{C}(\Pi_{uy}) | m_y | \tilde{X}(A_g) \rangle \right] \quad (7)$$

with the factor of 2 replacing the summation over the degenerate Π_u components. The prime on $\overline{A}_1'$ signifies that the matrix elements involve only the electronic part of the wavefunctions.

In order to relate the observed spectra to our theoretical results, we use the method of moments as applied to MCD and described by Stephens, Mowery, and Schatz (1971). The n^{th} moment of a MCD band can be defined as

$$\langle \Delta \epsilon \rangle_n = \int \frac{\Delta \epsilon}{E} (E - E^\circ)^n dE. \quad (8)$$

where E° is an average energy defined by $\langle \Delta \epsilon \rangle_1 = 0$. For the acetylene transition being studied here, the first moment is

$$\langle \Delta \epsilon \rangle_1 = .01525 \overline{A}_1' \quad (9)$$

with $\overline{A}_1'$ defined in Equation 7.

Finally, we need to obtain the vibrationally-averaged electric transition dipole moments between the two bound electron states in Equation 7. For this purpose, a section of the potential energy surface (PES) was calculated which approximates the normal mode describing the C-C symmetric stretch, with the vibrational coordinate, "R," being the C-C bond length. The C-H bond lengths are held fixed and the molecule remains linear. Using these PESs to calculate the vibrational wavefunctions $\chi_{v'}(R)$ and $\chi_v(R)$ for the $\Psi(\tilde{X})$ and $\Psi(\tilde{C})$ electronic wavefunctions, respectively, we

$$S(\tilde{X}; \tilde{C})_{v',v}^x = \langle \chi_{v'}(R) | \langle \tilde{X}(A_g) | m_x | \tilde{C}(\Pi_{ux}) \rangle | \chi_v(R) \rangle \quad (10a)$$

$$S(\tilde{C}; \tilde{X})_{v',v}^y = \langle \chi_{v'}(R) | \langle \tilde{C}(\Pi_{uy}) | m_y | \tilde{X}(A_g) \rangle | \chi_v(R) \rangle. \quad (10b)$$

The $\chi_v(R)$'s are obtained by numerically solving the radial Schroedinger equation for nuclear motion while ignoring rotational effects. The integrals in Equations 10a and 10b are then solved numerically using Simpson's rule.

The final forms for f and $\bar{A}_1$, which includes vibrational averaging, are

$$f_{v''v'} = \frac{2}{3} \Delta E \left\{ |S(\bar{X}; \bar{C})_{v''v'}^x|^2 + |S(\bar{C}; \bar{X})_{v''v'}^y|^2 \right\} \quad (11)$$

$$\bar{A}_{1(v''v')} = \frac{2Im}{3} \left\{ \langle \bar{C}(\Pi_{xz}) | \mu_z | \bar{C}(\Pi_{yz}) \rangle \cdot S(\bar{X}; \bar{C})_{v''v'}^x \cdot S(\bar{C}; \bar{X})_{v''v'}^y \right\}. \quad (12)$$

Note that the magnetic dipole transition moment in Equation 12 is a constant (i.e., one-half the orbital angular momentum quantum number for a Π state) with respect to the R(C-C) stretch and, therefore, excluded from the vibrational treatment.

3. DETAILS OF CALCULATIONS

The basis set used throughout this study consists of the primitives (11s.7p) contracted to [5s.4p] on the carbons and (6s) contracted to [3s] on the hydrogens (McLean and Chandler, unpublished results). The carbon atoms were augmented with two uncontracted d-type polarization functions and the hydrogens each received one uncontracted p-type function. To the center of the C-C bond was added a set of diffuse functions built up by first placing a diffuse p-function ($\alpha=0.018^6$) at the bond center. To this was added a single diffuse s-function whose exponent was chosen to optimize the energy of the $1^1\Pi_u$ state. The diffuse s- and p-functions were then split into two uncontracted functions using the prescription of Dunning (1977), and to this was added a single-component d-function (Peric, Buenker, and Peyerimhoff 1984), producing a (2s, 2p, 1d) set of diffuse orbitals. Each set of d-functions contain six angular momentum components, thus giving a total of 84 basis functions (details are given in Table 1).

The R(C-H) bond lengths were held constant at the experimentally determined ground state value of 1.058Å (Herzberg 1966). Henceforth all quantities shall be reported in atomic units unless stated otherwise. The PESs were calculated for the $\bar{X}(^1\Sigma_g^+)$ and $\bar{C}(^1\Pi_u)$ electronic states at the points R(C-C)=(1.783, 1.983, 2.083, 2.183, 2.283, 2.383, 2.483, 2.583, 2.783) in the reduced symmetry of the D_{2h} point group (both states have linear conformations) with the C-C bond as the z-axis. This section of the PES should be sufficient for estimating the dependence of the electric transition dipole moment on nuclear motion.

Table 1. Atomic Basis Set (McLean and Chandler)

<u>Carbon</u>		<u>Hydrogen</u>		<u>Diffuse</u>	
<u>Exponent</u>	<u>C.C.</u>	<u>Exponent</u>	<u>C.C.</u>	<u>Exponent</u>	<u>C.C.</u>
<u>1s</u>		<u>1s</u>		<u>1s</u>	
15469.40	0.000570	82.63637	0.002006	0.0304	1.0
2316.470	0.004388	12.40956	0.015345		
527.099	0.022810	2.823854	0.075577		
149.438	0.091563	0.797670	0.256922		
48.8562	0.290083				
17.62090	0.679184				
<u>2s</u>		<u>2s</u>		<u>2s</u>	
6.810820	0.637540	0.258053	1.0	0.012	1.0
2.7276	0.397545				
<u>3s</u>		<u>3s</u>			
0.756740	1.0	0.089891	1.0		
<u>4s</u>					
0.300730	1.0				
<u>5s</u>					
0.114090	1.0				
<u>1p</u>		<u>1p</u>		<u>1p</u>	
51.72330	0.009119	0.75	1.0	0.0342	1.0
12.33970	0.063253				
3.772240	0.269747				
1.32487	0.759674				
<u>2p</u>				<u>2p</u>	
0.505460	1.0			0.0135	1.0
<u>3p</u>					
0.198270	1.0				
<u>4p</u>					
0.077310	1.0				
<u>1d</u>				<u>1d</u>	
0.35	1.0			0.015	1.0
<u>2d</u>					
1.50	1.0				

The SA-CASSCF calculations were performed at each point on the PESs in order to generate a flexible set of orbitals for use in the CI calculations (Diffenderfer and Yarkony 1981). The CI calculations were performed with the ALCHEMY codes of Liu and Yoshimine (1981). A set of reference CSFs were used to generate the final CI expansions which consist of all single and double excitations relative to these reference CSFs. Further descriptions of the SA-CASSCF and CI calculations will be presented in the appropriate sections.

3.1 State Description. Since only singlet spin states are discussed in this study, the spin labels will be dropped from the state descriptions. In the ground state, the MO occupations are $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_{ux}^2 1\pi_{uy}^2$. The components of the $\tilde{C}$ state are represented by the MO fillings $\dots 1\pi_{ux}^2 1\pi_{uy}^4 \sigma_g^1$ and $\dots 1\pi_{ux}^1 1\pi_{uy}^2 4\sigma_g^1$, where the $4\sigma_g$ represents a s-Rydberg orbital. Based on these state descriptions, the active orbitals chosen for use in the SA-CASSCF consisted of the $1\pi_{ux}(1b_{3u})$, $1\pi_{uy}(1b_{2u})$, $4\sigma_g(4a_g)$, with the $4\pi_u$ electrons distributed in all possible ways amongst these orbitals. The weights, w_k , in Equation 1 were chosen to be (2,1,1) for $\tilde{X}$, $\tilde{C}(\Pi_{ux})$, and $\tilde{C}(\Pi_{uy})$, in that order. The resulting orbitals were then used as expansion vectors in the CI calculations.

The reference CSFs used for generating the CI wavefunctions are listed in Table 2. The sum of the squares of the CI coefficients, i.e., $\sum c_i^2$, for the reference set varies from 0.89 to 0.92 for $\tilde{X}$ and 0.90 to 0.93 for each $\tilde{C}$ component over the range of the PESs. Both the Π_{ux} and Π_{uy} components were calculated as an internal check on the symmetry of the wavefunctions. As an additional check, the magnetic transition dipole moment, $\langle \mu_z \rangle$, coupling Π_{ux} and Π_{uy} was calculated to be 0.5, which is correct for a Π state. † The total number of CSFs used to describe the electronic states are 29,509

†The actual expression representing the $\Delta\epsilon/E$ calculated in this study is given by

$$\frac{\Delta\epsilon}{E} = .01525 \left[\bar{A}_1 \left(\frac{\partial f}{\partial E} \right) \right] \cdot H$$

which differs from Equation 5 only in the units conversion due to the substitution of the orbital angular momentum operator for the magnetic dipole moment operator and carrying through the multiplication by μ_B , the Bohr magneton. The definition of $\bar{A}_1$ then becomes

$$\bar{A}_1 = \frac{Im}{3} \sum_{\lambda, \lambda'} \left[\langle \vec{I}_\lambda | \vec{L} | \vec{I}_{\lambda'} \rangle \cdot \langle \vec{X} | \vec{m} | \vec{I}_\lambda \rangle \times \langle \vec{I}_{\lambda'} | \vec{m} | \vec{X} \rangle \right].$$

where use has been made of the relationship $\vec{\mu} = (1/2)\vec{L}$.

Table 2. Reference CSFs Used in Generating in CI Wavefunctions

IRREP:	a_g	a_u	b_{1g}	b_{1u}	b_{2g}	b_{2u}	b_{3g}	b_{3u}
MO:	σ_g	δ_u	δ_g	σ_u	π_{gx}	π_{uy}	π_{gy}	π_{ux}

IRREP	$2\sigma_g$	$3\sigma_g$	$4\sigma_g$	$2\sigma_u$	$3\sigma_u$	$1\pi_{ux}$	$2\pi_{ux}$	$4\pi_{ux}$	$1\pi_{uy}$	$2\pi_{uy}$	$4\pi_{uy}$	$1\pi_{gx}$	$2\pi_{gx}$	$1\pi_{gy}$	$2\pi_{gy}$
$A_g(\Sigma_g^+)$	2	2	-	2	-	2	-	-	2	-	-	-	-	-	-
	2	2	-	2	-	2	-	-	-	-	-	-	-	2	-
	2	2	-	2	-	-	-	-	2	-	-	2	-	-	-
$A_u(\Sigma_u^-)$	2	2	-	2	-	2	-	-	1	-	-	1	-	-	-
	2	2	-	2	-	2	-	-	1	-	-	-	1	-	-
$B_{1u}(\Delta_u)$	2	2	-	2	-	1	-	-	2	-	-	1	-	-	-
	2	2	-	2	-	2	-	-	1	-	-	-	-	1	-
	2	2	-	2	-	1	-	-	2	-	-	-	1	-	-
	2	2	-	2	-	2	-	-	1	-	-	-	-	-	1
$B_{3u}(\Pi_{ux})$	2	2	1	2	-	1	-	-	2	-	-	-	-	-	-
	2	2	1	2	-	1	-	-	-	-	-	-	-	2	-
$B_{2u}(\Pi_{uy})$	2	2	1	2	-	2	-	-	1	-	-	-	-	-	-
	2	2	1	2	-	-	-	-	1	-	-	2	-	-	-
$B_{2g}(\Pi_{gx})$	2	2	-	2	1	1	-	-	2	-	-	-	-	-	-
	2	2	-	2	1	1	-	-	-	-	-	-	-	2	-
$B_{3g}(\Pi_{gy})$	2	2	-	2	1	2	-	-	1	-	-	-	-	-	-
	2	2	-	2	1	-	-	-	1	-	-	2	-	-	-
$B_{1g}(\Delta_g)$	2	2	-	2	-	1	-	-	2	1	-	-	-	-	-
	2	2	-	2	-	2	1	-	1	-	-	-	-	-	-
	2	2	-	2	-	1	-	-	2	-	1	-	-	-	-
	2	2	-	2	-	2	-	1	1	-	-	-	-	-	-

for the $\tilde{X}$, and 96,260 for each component of the $\tilde{C}$ state. The PESs resulting from the CIs are shown in Figure 1 and the values given explicitly in Table 3.

3.2 Vibrational Treatment. Effects of nuclear motion were included using an approximate symmetric stretch normal mode. For all the PESs the C-H bond lengths were held constant, and for the C-C stretch the vibrational wavefunctions were calculated by treating the molecule as a homonuclear diatomic. Two different estimates were used for the effective reduced mass for this mode. In the first approach, atomic masses of 13 were centered at each carbon atom, giving a reduced mass of 6.5 amu for both states. In the second approach, for each state the effective reduced mass of the system was taken to reproduce the experimental stretching fundamental, ν_2 . This predicts reduced masses of $\tilde{X}$ (7.15 amu) and $\tilde{C}$ (6.92 amu). The differences in reduced masses result in changes in the final MCD intensities from 2% in the 0-0 transition to 5% in the 0-3 transition which are certainly acceptable in the context of these calculations. All the vibrationally-averaged quantities reported in this T04850 study were obtained using the latter approach to approximating the nuclear masses.

4. RESULTS

The results from the vibrational analyses on the $\tilde{X}$ and $\tilde{C}$ states are summarized in Table 5, including the energies for the lowest four vibrational states. Gedanken and Schnepf assign the progression beginning at 65,860 cm^{-1} in their MCD and absorption spectra to the totally symmetric C-C stretch. This is to be compared to the calculated T_0 of 63,175 cm^{-1} .

Figure 2 includes the electric transition dipole moment as a function of $R(\text{C-C})$ and Table 4 lists these values. These are the first high quality calculations reported for these quantities as a function of C-C distance. The oscillator strengths obtained from vibrationally averaging these moments are given in Table 6. The sum of the f^{calc} values for the first four vibrational bands is 0.157. An early experimental determination of the oscillator strength by Moe and Duncan (1952) gave $f^{\text{Exp}}=0.0616\pm0.0092$. They qualify their number by stating that the experimental values might best be treated as a minimum value, while "...the true values may be much larger." A more recent experimental value of $f^{\text{Exp}}=0.110$ was extracted from the absorption spectrum of Gedanken and Schnepf. With this new value, the comparison between theory and experiment has improved considerably, but a discrepancy of 43% still remains between theory and experiment.

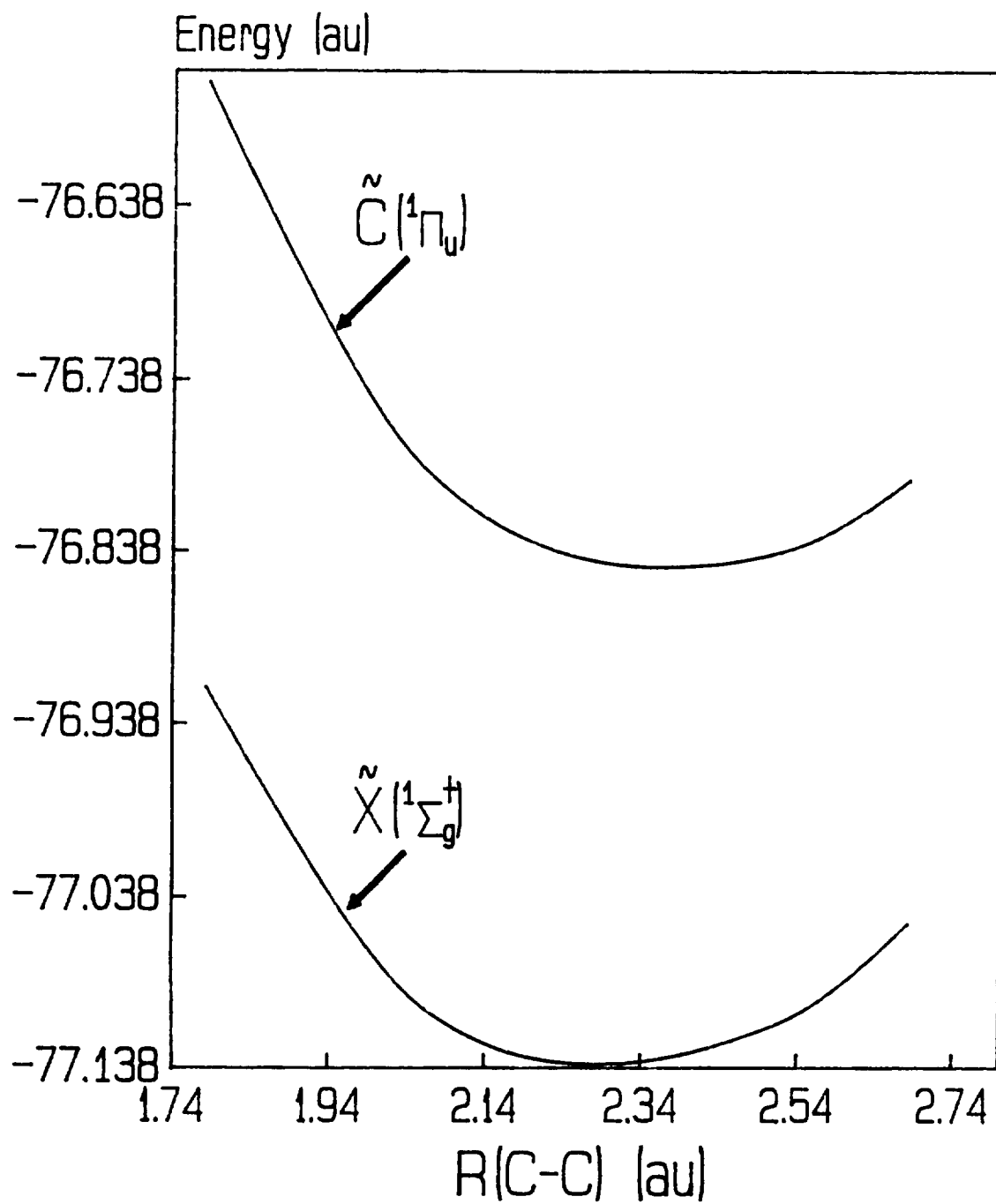


Figure 1. Sections of the Potential Energy Surfaces as a Function of C-C Distance for the $\tilde{\text{X}}(1^1\Sigma_g^+)$ and $\tilde{\text{C}}(1^1\Pi_u)$ States (All Values in au). The C-H Bond Lengths are Held Fixed at the Ground State Value.

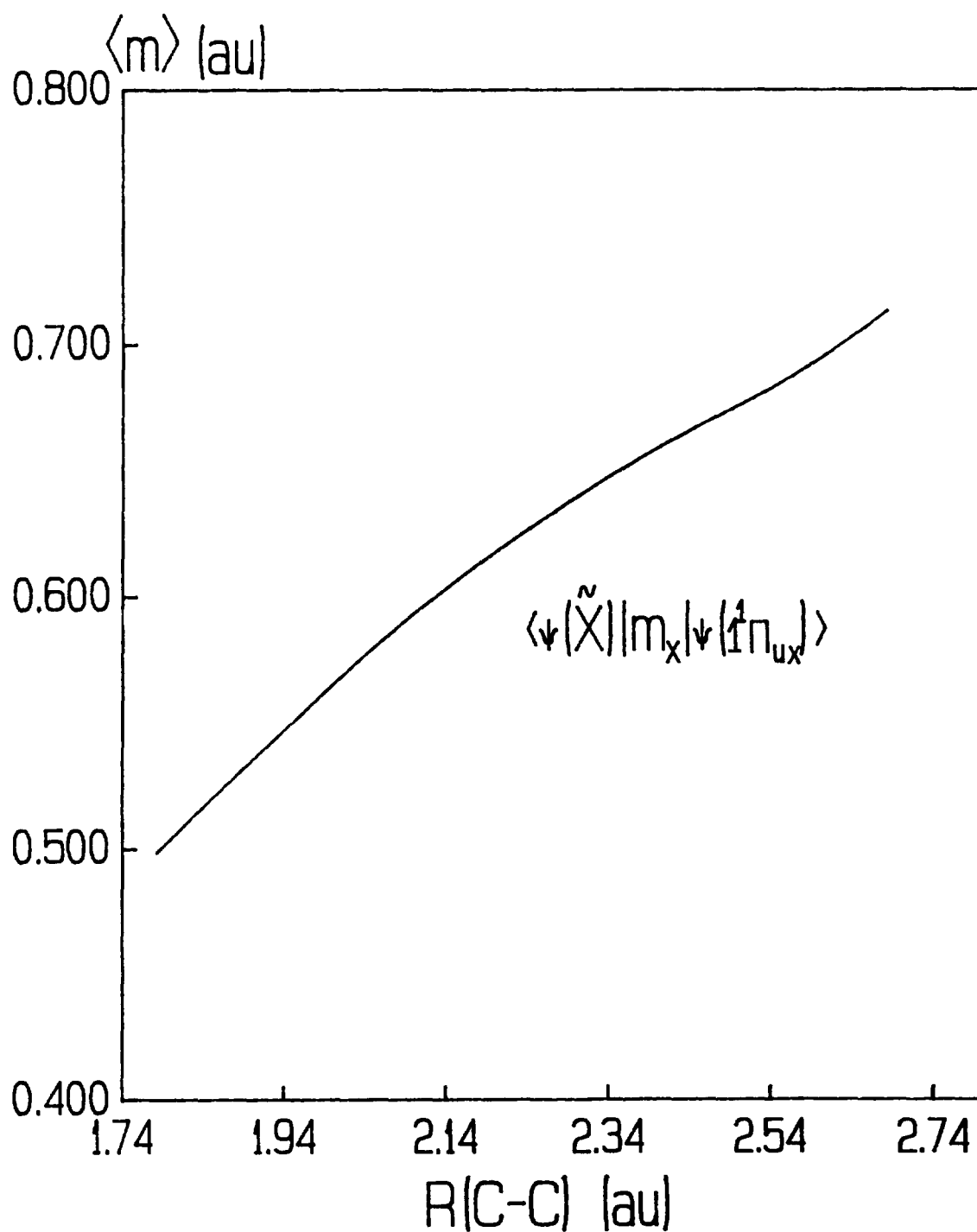


Figure 2. The X-Component of the Electric Dipole Transition Moment as a Function of C-C Distance. The Equilibrium C-C Bond Length is Given Experimentally to be 2.282 Bohr.

Table 3. $\tilde{X}$ and $\tilde{C}(^1\Pi_u)$ State Energies as a Function of C-C Bond Length

R(C-C) au	$\tilde{X}(^1\Sigma_g^+)$ au	$\tilde{C}(^1\Pi_u)$ au
1.78279	-76.91684	-76.56676
1.98279	-77.07607	-76.75395
2.08279	-77.11386	-76.80332
2.18279	-77.13276	-76.83253
2.28279	-77.13758	-76.84657
2.38279	-77.13202	-76.84926
2.48279	-77.11889	-76.84356
2.58279	-77.10039	-76.83175
2.78279	-77.05356	-76.79637

Table 4. Electric Transition Dipole Moment as a Function of R(C-C)

R(C-C) au	$\langle \Psi(\tilde{X}) m_x \Psi(\Pi_{ux}) \rangle^*$ au
1.7828	0.4983
1.9828	0.5616
2.0828	0.5891
2.1828	0.6139
2.2828	0.6362
2.3828	0.6560
2.4828	0.6734
2.5828	0.6886
2.6828	0.7129

* The magnitude of the $\tilde{\Pi}_{uy} \leftarrow \tilde{X}$ component is identical to at least the number of digits reported.

Table 5. Results of the Vibrational Analysis on the $\tilde{X}$ and $\tilde{C}$ States for the Symmetric C-C Stretch

<u>Predicted Vibrational Energies (cm⁻¹)</u>					
v	$\tilde{X}$		$\tilde{C}$		
0	988		921		
1	2955		2749		
2	4905		4563		
3	6829		6369		

ν_2 Fundamental ^a			T_0		
	$\tilde{X}$	$\tilde{C}$	Theory	63175	(7.83eV)
Theory	1977	1841	Exper.	65814	(8.16eV) ^b
Exper. ^b	1974	1840	Exper.	65860	(8.17eV) ^c

- a. The theoretical ν_2 obtained from varying the reduced mass of the system, and is defined as $\nu_2 = 2 \times E(v=0)$.
b. From Herzbert (1966).
c. From Gedanken and Schnepf (1976).

Table 6. MCD Intensities and Oscillator Strengths for Vibrational Bands in the $\tilde{C} \leftarrow \tilde{X}$ Transition

v''	v'	$\langle \Delta \epsilon \rangle_1^{\text{Calc}^a}$	$\langle \Delta \epsilon \rangle_1^{\text{Exp}^b}$	f^{Calc}	f^{Exp^c}	f^{Exp^d}	f^{Theory^e}
0	0	0.0179	0.0125±.001	0.1046	0.0743		
0	1	0.0068	0.0040±.0004	0.0408	0.0306		
0	2	0.0015	0.0007±.0001	0.0094	0.0046		
0	3	0.0003	0.0001±.00001	0.0017	0.0008		
TOTAL		0.0265	0.0173	0.1565	0.1103	0.0616 .0092	0.072

- a) Reduced mass determined by fitting calculated ν_2 to experiment. See text for details.
b) From Gedanken and Schnepf (1976).
c) Calculated from the $\mathcal{D}_0$ values listed in Table 2 of Gedanken and Schnepf (1976). These $\mathcal{D}_0$ were extracted by Gedanken and Schnepf from their absorption spectrum after subtracting out intensity from an unassigned, underlying band.
d) See Moe and Duncan (1952).
e) From *ab initio* "frozen core" calculations. Includes no correlation corrections. See Demoulin and Jungen (1974).

The MCD spectrum provides another independent check on the electric transition dipoles. The calculated and experimental MCD intensities for the first four vibrational bands are also given in Table 6. The agreement is qualitatively correct, showing decreasing MCD intensity with the increasing v' . One finds reasonably good agreement between experiment and theory for the 0-0 transition where theory and experiments predict $\langle\Delta\epsilon\rangle_1=0.0179$ and $0.0125\pm.001$, respectively. Again, the theory predicts an intensity that is 43% larger than experiment; consistent with the difference seen in absorption. The reader should be reminded that the same electric dipole moments are used in the theoretical predictions of the oscillator strength and the MCD intensities. This consistency in the comparisons between theory and experiment for absorption intensities and MCD intensities supports the experimental correction to the absorption intensity achieved by subtracting out the broad band underlying the experimental absorption spectrum. The values for the 1-0, 2-0, and 3-0 bands are (theory,experiment)=(0.0068,0.0040)₁₀, (0.0015,0.0007)₂₀, (0.0003,0.0001)₃₀. All the calculated values are seen to be larger than their experimental counterparts. Assuming the experimental MCD values are accurate, the fact that the lower v' levels agree better with experiment than the higher v' levels suggests increasing inaccuracies in the Franck-Condon overlap with these higher vibrational levels. This in turn would indicate that the $\tilde{C}$ state PES is not described with equal accuracy over the range of the PES section studied. Specifically, the PES seems better described near the equilibrium, $R(C-C)$.

5. CONCLUSIONS

This is the first report using a large atomic basis set and large CI expansions to predict *a priori* the electric dipole transition moment for the $\tilde{C}\leftarrow\tilde{X}$ band system as a function of $R(C-C)$. The calculated $T_0=63,175\text{ cm}^{-1}$ is in reasonable agreement with the experimental value of $65,860\text{ cm}^{-1}$. An approximate vibrational averaging of the electric transition dipole moment predicts an absorption oscillator strength of $f=0.157$, which is more than a factor of 2 larger than an early experimental value of $f=0.062\pm.0092$, but in better agreement with a more recent value of 0.110 extracted from the experimental absorption spectrum of Gedanken and Schnepf (1976).

The experimental MCD intensities for the $\tilde{C}\leftarrow\tilde{X}$ transition was also used as another check on the calculated electric transition dipole moment. The advantage of using the MCD over the absorption is the apparent lack of interference in the band structure from a broad band present in the absorption. The integrated MCD intensity, $\langle\Delta\epsilon\rangle_1$, for the 0-0 transition is predicted to be 0.0179, which can be compared to the experimental value of $0.0125\pm.001$. Theory also predicts the correct trend of

decreasing MCD intensity for transitions to the higher v' levels of $\tilde{C}$, even though the difference between theory and experiment for $\langle \Delta \epsilon \rangle_1$ increases with increasing v' . The remaining discrepancy of approximately 40% between theory and experiment in both the MCD and absorption intensities suggests the need for more experimental work.

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