J. Phys. Chem. A **2007,** *111,* 4711−4713 **4711**

Intensity of d−d Symmetry-Forbidden Electronic Transition in Cr(CO)$_6$

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Received: January 15, 2007; In Final Form: March 19, 2007

Absolute absorption intensities (oscillator strengths) are calculated for the d−d symmetry-forbidden transition in hexacarbonyl chromium. The vibronic coupling mechanism is taken into account in a way that represents an alternative to the traditional perturbative approach of Herzberg and Teller. In the so-called direct method, the electronic transition moment is directly expanded in a power series of the vibrational normal coordinates of suitable symmetry. In the present case, i.e., d−d ligand field transitions, or more specifically $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, the dipole selection rule is broken by vibronic interaction induced by normal modes that transform like T_{1u} and T_{2u} representations of the O_h group. An analysis of the relative importance of normal modes in promoting electronic transitions is carried out.

I. Introduction

The electronic structure of hexacarbonyl compounds, M(CO)$_6$ (M = Cr, Mo, W), has long been studied by either experimental or theoretical approach. Their spectra are dominated by two very intense absorption bands at 4.43 and 5.41 eV, which were identified as $^1A_{1g} \rightarrow {}^1T_{1u}$ metal-to-ligand charge transfer spin-allowed transitions by Beach and Gray.[1] Additionally, a shoulder is observed at a lower energy (3.9 eV), and another one at 4.85 eV; this last one lies between the first and second charge-transfer bands. These shoulders were assigned as vibrational components of the ligand field $^1T_{1g}$, $^1T_{2g}$ ($t_{2g}{}^5e_g{}^1$) excited states by Beach and Gray. This assignment was accepted for a long time, but Pierloot et al.[2] have proposed a new assignment for Cr(CO)$_6$ based on a high-level quantum chemical calculation, namely, CASSCF/CASPT2. The main difference was found for the ligand field excited states, which appeared at a higher energy than that suggested by Beach and Gray. Pierloot et al. have pointed out that the shoulder at 4.85 eV corresponds to the transition from the ground state to the $^1T_{1g}$ ligand field (LF) state. According to their calculation, the $^1T_{2g}$ LF state is localized at 5.08 eV. Rosa et al.,[3] by means of relativistic TDDFT approach, have confirmed the results of Pierloot et al. for Cr(CO)$_6$ and have found similar results for the other members of the series, Mo(CO)$_6$ and W(CO)$_6$. The main conclusion of both works is that the lowest excited states in the spectra do not correspond to ligand field transitions, but correspond to charge-transfer (CF) states. More recently, Ben Amor et al.[4] have performed calculations for the lowest lying states of Cr(CO)$_6$ at several levels of theory, including equations of motion coupled cluster (EOM-CCSD) and multistate CAS perturbation theory at second order (MS-CASPT2), and confirmed the previous results. Hummel and co-workers[5] have found that the same picture holds for other species isoelectronic to Cr(CO)$_6$, i.e., V(CO)$_6{}^-$ and Mn(CO)$_6{}^+$.

The works cited above[2−4] have reported calculated oscillator strengths for dipole-allowed charge-transfer transitions. As is well-known, LF (d−d) transitions in octahedral compounds are the most prominent example of transitions forbidden by symmetry, which become allowed by coupling with vibrational modes of suitable symmetry. In the present case, $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions can become allowed by coupling to T_{1u} and T_{2u} vibrational modes. This mechanism is also known as intensity borrowing. Therefore, these transitions are electronically forbidden but vibronically allowed.

The present work complements the aforementioned scenario by reporting calculated oscillator strengths to $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ ligand field transitions in Cr(CO)$_6$. The method of calculation is the direct vibronic coupling,[6] which we have used successfully several times,[6−11] and which represents an alternative to the perturbation approach of Herzberg and Teller.[12] To the best of our knowledge, this kind of calculation in a transition metal compound is being reported for the first time.

This discussion is also relevant to the photodissociation of Cr(CO)$_6$. A mechanism has been proposed[13] in which a ligand field state is responsible for dissociation, leading to CO elimination. The results agree reasonably well with time-resolved experimental studies.[14]

II. Theoretical Background

The theoretical procedure used in the present calculations was discussed in detail elsewhere.[6] Briefly, we start from the expression for the optical oscillator strength:

$$f = \frac{2}{3}Eg_k|\langle\chi_{kv}|M|\chi_{00}\rangle|^2 \tag{1}$$

where χ_{00} is the vibrational function of the electronic ground state and χ_{kv} is the vth vibrational function of the kth electronic state. E and g_k stand respectively for the transition energy and the degeneracy of the final state. M is the transition moment involving the ground and excited electronic states.

$$M = -\langle\psi_k(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_n;\mathbf{R})|\sum_i \mathbf{r}_i|\psi_0(\mathbf{r}_1,\mathbf{r}_2,...,\mathbf{r}_n;\mathbf{R})\rangle \tag{2}$$

Summing eq 1 over all vibrational states of the excited electronic state and expanding the squared dipole transition

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10.1021/jp070334b CCC: $37.00 © 2007 American Chemical Society
Published on Web 04/27/2007

TABLE 1: Comparison of Calculated and Experimental Vibration Frequencies of Modes T_{1u} and T_{2u}

mode	calcd freq, present work	exptl freq[16]
ν_{13}	66.60	67.9
ν_9	106.77	97.2
ν_8	443.57	440.5
ν_{12}	525.34	510.9
ν_7	689.79	668.1
ν_6	2082.29	2000.4

moment in power series of the normal coordinates of vibrational motion, we arrived at

$$f = \frac{2}{3} E g_k \langle \chi_{00} | M^2(Q) | \chi_{00} \rangle \qquad (3)$$

with

$$M^2(Q) = |M(0)|^2 + \sum_L \sum_j a_j (Q_L)^j \qquad (4)$$

To get expression 4, transition moments are directly calculated along each of the L normal modes, followed by fitting to a polynomial function of order j in Q_L. Consequently, integration of expression 3 becomes straightforward.

The first term in the right-hand side of eq 4 represents the transition dipole moment calculated at equilibrium geometry. If the transition is dipole-allowed, this is the main contribution. On the other hand, if it is dipole-forbidden, the intensity is entirely due to terms in the double summation. The summation is performed over all normal modes L of suitable symmetry.

III. Results

The geometry was optimized and the vibrational frequencies were calculated at the DFT/B3LYP level with a 6-31G* basis set for carbon and oxygen and the effective core potential SBKJC for chromium. From now on, this will be called basis set I (BSI). The calculated bond distances were 1.93 Å for Cr−C and 1.15 Å for C−O, which must be compared to the experimental values 1.92 and 1.14 Å.[15] Table 1 shows the calculated vibrational frequencies for T_{1u} and T_{2u} normal modes. The agreement with experimental values[16] is good.

The same basis set was used to compute transition energies and moments. In principle, the basis set is not large enough to compute excited-state properties, so in order to investigate the limitation of BSI, another basis set was used to compute transition moments; the model core potential IMCP-SR2 of Lovallo and Klobukowski and its accompanying basis set[17] was the choice. We will refer to that as basis set II (BSII). Calculations with BSII were done at the same geometries as those done with BSI. BSII is considerably larger than BSI. The intention here is not to compute accurately all spectra, but to compute only the LF states, which are clearly valence states. In view of that, diffuse functions were not included in the basis set. A larger basis in the valence would be computationally expensive, since one cannot use the full symmetry of the O_h group, given that the transition moments had to be calculated at distorted geometries of the molecule, following the vibrational modes of T_{1u} and T_{2u} symmetry. There are six (triply degenerated) normal modes of such types in $Cr(CO)_6$, and if, for example, the transition moment is calculated at five points along each normal mode in order to fit the function given in eq 4, one ends with 90 single-point calculations for each basis set. Thus, time is a matter of some concern in the choice of basis set. All calculations were done with the GAMESS package.[18]

The transition energy was calculated at ground-state geometry within the CASSCF (10,10)[19,20] averaged over the states and multiconfiguration quasi-degenerate perturbation theory (MCQDPT).[21] The active space was composed by the orbitals $2t_{2g}$, $3t_{2g}$, $5e_g$, and $6e_g$. Pierloot et al.[2] have shown that this active space is suitable to describe these LF transitions. Table 2 shows the calculated transition energies at MCQDPT compared to other calculations. One can see that there is a good agreement of the present calculation and the CASPT2 calculations of Pierloot et al., which have used a much large basis set of (17s12p9d4f)/[6s4p3d1f) for Cr and (10s6p3d)/[3s2p1d] for C and O. This shows that, at least for the states considered here, the basis set chosen seems to be adequate.

Oscillator strengths were obtained from transition moments calculated at the CASSCF (10,10) level and transition energies calculated at the MCQDPT level. The results are shown in Table 3 for $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions. Beach and Gray have reported values for the oscillator strength to the allowed transition at 4.43 and 5.48 eV to be 0.25 and 2.3 respectively, and a value of 0.037 for the oscillator strength of the shoulder at 4.83 eV, which is almost an order of magnitude higher than that of the present work, 0.00522. In this matter, one has to consider that it is quite strange that an intensity borrowing mechanism could result in an oscillator strength that is about 15% of the value for the allowed transition. Therefore, the value reported by Beach and Gray (0.037) seems to be quite large.

TABLE 2: Comparison of Transition Energies for Ligand Field States Calculated by Several Methods[a]

transition	EOM-CCSD[4]	MS-CASPT2[4]	CASPT2[2]	TDDFT[3]	MCQDPT (BSI)	MCQDPT (BSII)
$^1A_{1g} \rightarrow {}^1T_{1g}$	5.15	4.60	4.85	5.20	4.85	4.85
$^1A_{1g} \rightarrow {}^1T_{2g}$	5.58	4.91	5.08	5.61	5.47	5.50

[a] Present results are shown for both basis sets BSI and BSII (see text).

TABLE 3: Per Mode Contributions to Oscillator Strength for d−d Transition, Calculated by Direct Vibronic Coupling Mechanism[a]

mode	symmetry	*f*(BSI)[b]	*f*(BSII)[b]	*f*(BSI)[c]	*f*(BSII)[c]
ν_{13}	T_{2u}	1.16×10^{-4}	1.26×10^{-4}	1.08×10^{-4}	1.02×10^{-4}
ν_9	T_{1u}	2.08×10^{-5}	1.80×10^{-5}	4.18×10^{-6}	4.21×10^{-6}
ν_8	T_{1u}	1.22×10^{-3}	1.10×10^{-3}	8.15×10^{-4}	6.78×10^{-4}
ν_{12}	T_{2u}	1.20×10^{-3}	1.03×10^{-3}	7.17×10^{-5}	4.33×10^{-5}
ν_7	T_{1u}	2.61×10^{-3}	2.29×10^{-3}	5.08×10^{-5}	5.65×10^{-5}
ν_6	T_{1u}	7.69×10^{-4}	6.59×10^{-4}	9.55×10^{-5}	9.26×10^{-5}
total		5.94×10^{-3}	5.22×10^{-3}	1.15×10^{-3}	9.77×10^{-4}

[a] Results are shown for two basis sets. [b] $^1A_{1g} \rightarrow {}^1T_{1g}$ transition. [c] $^1A_{1g} \rightarrow {}^1T_{2g}$ transition.

Another point to be considered is that their spectra are not well resolved and this transition appears as a weak shoulder in the spectrum, which could lead to major errors. On the other hand, the method used in the present work to calculate the vibronic coupling has been used quite successfully in other cases,[6−11] particularly in some carbonylated compounds, such as formaldehyde and acetone, in which the forbidden n → π^* transition appears isolated in the spectrum. This transition is vibronically allowed and the method used here led to very good agreement with experimental values, in spite of the small value for the oscillator strength.

Table 3 shows that the main contribution to the oscillator strength for the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition comes from modes related to Cr−C−O bending (ν_{12} and ν_7), about 64% and the Cr−C bond stretching mode (ν_8), about 21%. Thus, these modes are expected to be excited if the $^1T_{1g}$ state is formed by direct irradiation. Additionally, Table 3 reveals that the most import contribution to the intensity of $^1A_{1g} \rightarrow {}^1T_{2g}$ transition comes from the Cr−C stretching mode ν_8. It is interesting to note that C−Cr−C bending modes (ν_{13} and ν_9) show only minor contributions to both transitions. The same is true for the CO stretching mode ν_6. This last case is quite expected, since this is a ligand field or metal-centered transition. The same is not true for C−Cr−C bending modes that were expected to be more effective in promoting photon absorption through a vibronic coupling mechanism.

IV. Conclusion

Oscillator strengths were calculated for the d−d ($^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$) symmetry-forbidden transition in $Cr(CO)_6$ by means of a direct vibronic coupling mechanism. These transitions are made vibronically allowed through the vibrational modes of T_{1u} and T_{2u} symmetry in the O_h group. An analysis of the relative importance of normal modes showed that the main contribution to the oscillator strength for the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition comes from modes related to Cr−C−O bending (ν_{12} and ν_7), about 64%, and the Cr−C bond stretching mode (ν_8), about 21%. Therefore, these modes are expected to be excited if the $^1T_{1g}$ state is formed by direct irradiation. Following the mechanism proposed in ref 13, the photodissociation of $Cr(CO)_6$ takes place on this state. The steps are, first, excitation from the ground state to the metal-to-ligand charge transfer ($^1A_{1g} \rightarrow {}^1T_{1u}$) state, then nonradiative decay to LF state, and finally the dissociation. The present study suggests that the direct irradiation of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition would lead the excited state to be formed vibrationally excited in the Cr−C−O bending and Cr−C bond stretching modes. Whether this could lead to any change in the dissociation mechanism would be a matter for a separate investigation. In the $^1A_{1g} \rightarrow {}^1T_{2g}$ transition the main inducing mode is the Cr−C stretching mode ν_8. It is worth mentioning that the C−Cr−C bending modes (ν_{13} and ν_9) only show minor contributions to both transitions, different from what would be expected on qualitative grounds.

Acknowledgment. The author would like to acknowledge Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and FAPERJ for financial support.

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