Investigation of the Reaction Coordinate for Dissociation in Cr(CO)₆ Using Resonance Raman Spectroscopy

Soo-Chang Yu*, Seuk-Beum Ko†, and J. B. Hopkins

*Department of Chemistry, Kunsan National University, Chonbuk 573-701, Korea

†Department of Chemistry, College of Chemical Education, Chonbuk National University, Chonbuk 560-756, Korea

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, U.S.A.

Received June 22, 1995

The overtone of the ν_2 vibrational mode in Cr(CO)₆ are observed for the first time in cyclohexane and methanol at both the 266 and 213 nm excitations. The appearance of the overtones due to the displacement of the electronic excited state with respect to the ground state along the ν_2 vibrational mode is interpreted in terms of wavepacket concept and molecular orbital (MO) theory. Our Raman results suggest a new interpretation for the excited state potential.

Introduction

The group VI transition metal carbonyl complexes have been the prototype molecules for understanding organometallic bonding and electronic structure. Cr(CO)₆ is one of the well-studied transition metal complexes.[1~3] Recent developments in laser technology now makes it possible to study ultrafast dynamics following photoexcitation.[4~8]

Upon photodissociation of Cr(CO)₆, Cr(CO)₅ is produced within 1 ps in the condensed phase and then the naked Cr(CO)₅ undergoes solvent coordination giving rise to the solvated Cr(CO)₅ as a final product.[4] UV-visible transient absorption,[4,6,7] transient IR[5] and transient Raman[8] spectroscopic techniques have been employed to investigate ultrafast phenomena occuring in the solution phase.

In order to predict the photochemical pathway from Cr(CO)₆ to the naked Cr(CO)₅, Raman spectroscopy of the ground state has been utilized since the Raman overtone of any vibrational mode in Cr(CO)₆ is a projection of the electronic excited state[2,6] onto the ground state. Any observed overtone progression implys a displacement of the electronic excited state along that vibrational mode. The appearance of the overtones of the ν_2 mode in Cr(CO)₆ is of interest in that it provides information on the shape of the potential energy surface of the electronic excited state; thus the possibility of that mode being the reaction coordinate on which the bond breakage between the chromium and carbonyl group occurs. We observed for the first time the overtones of the ν_2 mode in Cr(CO)₆ at the 266 and 213 nm excitations using Raman spectroscopy.

Experimental

The experimental apparatus has been previously described in detail.[9] The laser system consists of a high repetition rate (2 kHz) chirped pulse regenerative amplifier which provides 1 mJ pulses at 1.06 μm. A mode locked cw Nd : YAG laser in combination with a single mode optical fiber is used to produce the seed pulse to the regenerative amplifier. Following grating compression the output pulse of this laser has an 8 ps temporal duration. In this experiment the time resolution of the apparatus is irrelevant since only normal Raman scattering is detected. Laser excitation occurs in a free flowing jet which moves the solution at a speed sufficient to ensure that no two successive pulses interrogate the same region of sample. Raman scattering is dispersed by an ISA U1000 double monochromator. The signal is detected by a photomultiplier tube, and processed by a gated integrator.

Cr(CO)₆ was purchased from Aldrich and used without further purification. The concentration was 10 mM in cyclohexane and methanol. Cyclohexane was purchased from Aldrich and was of spectrograde purity. Methanol was HPLC grade and purchased from Mallinckrodt.

Results and Discussion

Cr(CO)₆ has 33 normal vibrational modes. The representation of 33 vibrational modes is reduced to 13 fundamentals[10] by $F = 2A_{1g} + 2E_g + T_{1g} + 4T_{1u} + 2T_{2g} + 2T_{2u}$. Among the Raman active modes, the ν_1 and ν_2 modes belong to the totally symmetric A_{1g} representation, and the rest belong to the nontotally symmetric vibrational modes. Two different Raman excitation wavelengths of 266 and 213 nm were used in our experiment. The 266 nm wavelength is off resonance and the 213 nm wavelength is in resonance with the second charge transfer (C-T) transition.[2] In view of symmetry considerations it is expected that two different types of vibrational modes will be enhanced depending on the excitation. The experimental data shown in Figure 1 indicate that the non-totally symmetric vibrational modes, ν_{10} (M-C-O bending) and ν_3 (C-O stretching), are enhanced by the 266 nm excitation. On the other hand, the totally symmetric vibrational modes, ν_2 (M-C stretching) and ν_1 (C-O stretching, shown in Figure 2), are enhanced by the 213 nm excitation.

One overtone of the ν_2 mode, 0-2 is observed at 760 cm⁻¹ in both spectra; it is unlikely that the overtones of the ν_2 vibrational mode appear at the 266 nm excitation considering that the totally symmetric vibrational modes are resonantly enhanced only at the dipole-allowed transitions. In fact, it is not easy to assign overtones because the vibrational anharmonicities are not known at this time. Nonetheless, these bands are assigned to overtones with confidence by com-

---

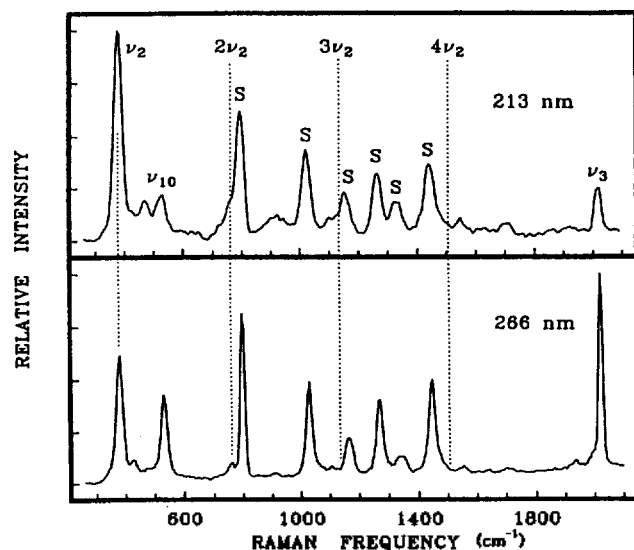**Figure 1.** Raman spectra of Cr(CO)$_6$ in cyclohexane were taken at the 266 and 213 nm excitations. The overtones of the ν_2 mode appear in both the 266 and 213 nm excited sepctra. The overtones appear to be enhanced at the 213 nm excitation as expected from the vibronic theory. These overtones are confirmed by matching each other at two different excitations. $2\nu_2$ stands for the 0-2 overtone of the ν_2 mode. Likewise, $3\nu_2$ stands for 0-3, and $4\nu_2$, 0-4 overtone, respectively. The cyclohexane solvent bands are represented by S.
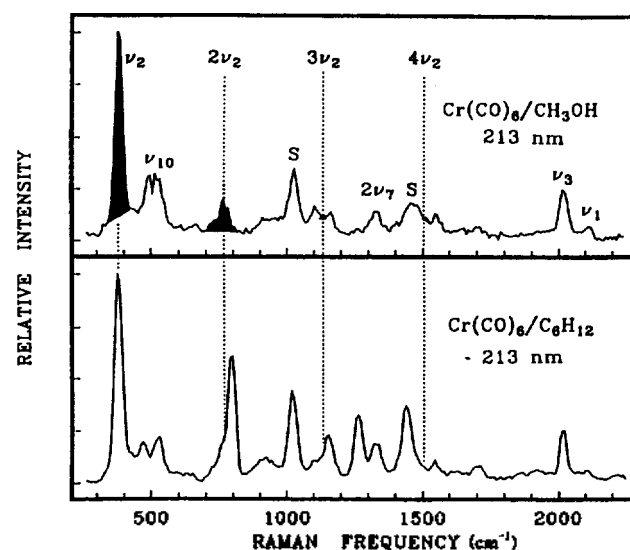

Figure 2. Raman spectra of Cr(CO)$_6$ were obtained in two different solvents under the same conditions. The overtones of the ν_2 mode appear in both solvents. The ambiguity of the overtones in cyclohexane is clarified by comparing them with those in methanol. Especially, the $2\nu_2$ mode in methanol is apparent without being interfered by any solvent bands. The ν_1 mode also appears to be enhanced at the 213 nm excitation compared to the 266 nm excitation implying that C-O is also displaced as expected from the vibronic theory.

paring the relative intensities between two spectra. The enhancement of the fundamental of the ν_2 mode is much larger in the 213 nm excited spectrum than in the 266 nm one. This is also true for the overtones, 0-2, 0-3, and 0-4 (0-3 and 0-4 overtones are not so apparent as 0-2 overtone, but this fact does not affect our conclusion). These overtones are not apparent in Figure 1 because of the interference of the cyclohexane solvent bands. However, they are clear in the spectrum taken in the methanol solution as shown in Figure 2.

This result is in contrast to that of Gerrity *et al.*[2] in that their spectra did not show these overtones at the 253, 266, and 281 nm excitations in the same solution. However, in our spectrum by matching the overtones in the 266 nm excited spectrum with those in the 213 nm excited spectrum, it is confirmed that the overtones in the 266 nm excited spectrum are not due to any artifacts. According to the theory the overtones of the ν_2 mode are not supposed to appear in the 266 nm spectrum became the 266 nm excitation corresponding to the dipole-forbidden d-d transition does not enhance the totally symmetric ν_2 mode. The overtones of a particular mode, however, can appear even in a dipole-forbidden transition only if the excited state is displaced with respect to the ground state along that vibrational mode. This can be better understood by considering the wavepacket description.[12−13] If we promote the wavepacket from the electronic ground state to the excited state at time zero ($t = 0$) using the sudden approximation, the initial excited state is the same as the ground state wavefunction. As it evolves with time, the wavefunction overlaps with higher vibrational states. For a given vibrational progression, the

overlap will develop continuously from the lowest vibrational level to the higher level, depending on the extent of displacement of the vibrational coordinate in the excited state.

The appearance of the overtones of the ν_2 mode at the 266 nm excitaion is an indication that the excited state is displaced relative to the ground state along this normal mode. This reasoning does make sense in considering an electronic transition in terms of molecular orbital (MO) theory. The transition ($1A_{1g}$-$1T_{1g}(\sigma^*)$) corresponding to the 266 nm excitation accompanies one electron transition from the non-bonding $d(\pi)$ orbital in t_{2g} electronic state to the anti-bonding $d(\sigma^*)$ orbital in e_g electronic state. The transition from the non-bonding to the anti-bonding orbital results in two effects which decrease the bonding properties. The π backbonding decreases when one electron is removed from a lone pair $d(\pi)$ orbital in the t_{2g} electronic state. The bonding is also reduced by population of the σ^* antibonding orbital. These two cooperative effects cause the weakening the bond between metal and carbonyl group. The displacement of the metal and carbonyl group in the excited state accounts for the appearance of the overtones for the totally symmetric mode in this transition.

In the 213 nm exaited Raman spectrum the totally symmetric mode, ν_2, is enhanced by a factor of 3-4 compared to that in the 266 nm excited spectrum. The 213 nm transition corresponding to the $1A_{1g}$-$1T_{1u}(\pi^*)$ transition is different from the 266 nm one in that the former is strongly dipole-allowed whereas the latter is forbidden d-d transition. The depopulation of the non-bonding $d(\pi)$ orbital and the population of the π^* CO in t_{2u} electonic state are the sources for the displacement of the M-CO as well as the C-O bonding.
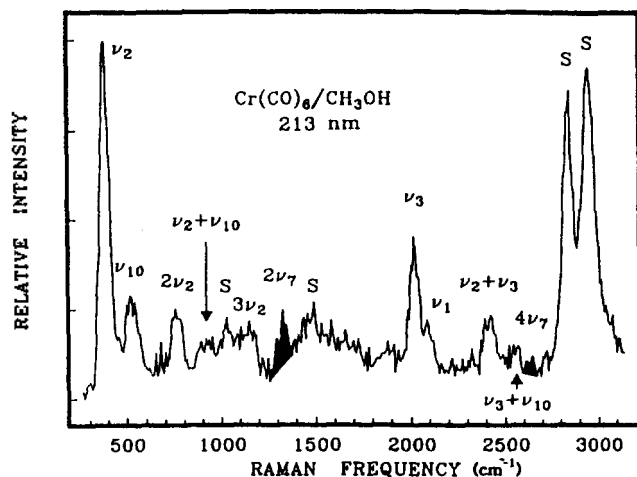
Figure 3. Raman spectrum of Cr(CO)₆ in methanol was taken at the 213 nm excitation. The bands for the 0-2 and the 0-4 overtone of the v_7 mode are blackened at the center of approximately 1330 and 2625 cm⁻¹, respectively. There are also several overtones of the v_2 appeared with its combinations. The methanol solvent bands are represented by S.

As in the case of the 266 nm excitation, the depopulation of the non-bonding $d(\pi)$ decreases the strength of π backbonding, thus reduces the M-CO bond. On the other hand, population of the anti-bonding orbital of the π^*CO decreases the strength of the C-O bonding. In such a case, the displacement of the C-O bond will take place. As a result, at the 213 nm excitation the displacement of both M-CO and C-O bond can be observed. In order for a reaction to occur a bond has to be displaced largely along a particular vibrational mode just before a breakage. Conversely, if a large displacement of bond occurs along a particular vibrational mode, that mode can be a reaction coordinate. The evidence for a reaction coordinate is the appearance of the overtones in the resonance Raman spectrum.

It is interesting to compare the v_2 vibrational mode with the v_7 vibrational mode of which 0-2 overtone is also reported by Nelson et al.[6] They observed the 0-2 overtone of the v_7 mode around 1332 cm⁻¹ and referred to it as the reaction coordinate; the fundamental of the v_7 at 665 cm⁻¹ is reported elsewere.[14] The difference between two vibrational modes is that the v_2 mode belongs to the totally symmetric mode, whereas the v_7 mode belongs to the non-totally symmetric mode. Therefore, all of six carbonyl groups are equally elongated by the same amount during the totally symmetric vibrational motion, but not all of them are equally elongated during the non-totally symmetric vibrational motion. In view of the fact that all six carbonyl groups are unlikely to be largely displaced by the same amount during the reaction, Nelson et al.[6] prefered the v_7 mode to the v_2 mode as the reaction coordinate. The appearance of the higher overtones such as the 0-4, 0-6 of the v_7 mode, however, would confirm it being the reaction coordinate with confidence. As a matter of fact, this argument is well supported by our finding of

the higher overtones. As can be seen in Figure 2 and Figure 3, two v_7 overtones corresponding to 0-2 and 0-4 appear to exist around 1330 and 2625 cm⁻¹, respectively. According to our knowledge the 0-4 overtone is observed for the first time in this experiment.

Admitting the v_7 mode to be the reaction coordinate, the role of the v_2 mode is now in question. The v_2 mode seems to be coupled with the v_7 mode, so that the initial excitation involves the low frequency mode, the v_2, in the excited state and then this electronic state undergoes nonradiative relaxation to the dissociative state generated by the vibration of the v_7 mode, from which the reaction occurs. The significance of this result lies in that the existence of the v_2 overtones is probably the evidence for the initial excitation of the low frequency mode which finally undergoes nonradiative relaxation to the high frequency mode, the v_7, by coupling.

Conclusion

We observed for the first time the overtones of the v_2 vibrational mode at both the 266 and 213 nm excitations using Raman spectroscopy. The appearance of the overtones is interpreted in view of the wavepacket concept and the MO theory, and is concluded that the displacement of the electronic excited state with respect to the ground state along the v_2 is involved at both the 266 and 213 nm excitations. Resonance Raman spectroscopy is proven to be a useful technique to obtain information on the intermediate species with the help of the overtones of certain vibrational modes.

References

1. Burdet, J. K.; Grzybowski, J. M.; Perutz, R. N.; Poliakoff, M.; Turner, J. M.; Turner, R. F. *Inor. Chem.* 1975, *14*, 1058.
2. Adelman, D.; Gerrity, D. P. *J. Phy. Chem.* 1990, *94*, 4055.
3. Wrighton, M. *Chem. Rev.* 1974, *74*, 401.
4. Simon, J. D.; Xie, X. *J. Phy. Chem.* 1986, *90*, 6751.
5. Wang, L.; Zhu, X.; Spears, K. G. *J. Am. Chem. Soc.* 1988, *110*, 8695.
6. Joly, A. G.; Nelson, K. A. *Chem. Phys.* 1991, *152*, 69.
7. Lee, M.; Harris, C. B. *J. Am. Chem. Soc.* 1989, *111*, 8963.
8. Yu, S.-C.; Xu, X.; Lingle, R. Jr.; Hopkins, J. B. *J. Am. Chem. Soc.* 1990, *112*, 3668.
9. Chang, Y. J.; Xu, X.; Yabe, T.; Yu, S.-C.; Anderson, D. R.; Orman, L. K.; Hopkins, J. B. *J. Phys. Chem.* 1990, *94*, 729.
10. Hawkins, N. J.; Mattraw, H. C.; Sabol, W. W.; Carpenter, D. R. *J. Chem. Phys.* 1955, *23*, 2422.
11. Albrecht, A. C. *J. Chem. Phys.* 1961, *34*, 1476.
12. Lee, S. Y.; Heller, E. J. *J. Chem. Phys.* 1982, *76*, 3035.
13. Imre, D.; Kinsey, J. L.; Sinha, A.; Krenos, J. *J. Phys. Chem.* 1984, *88*, 3956.
14. Jones, L. H.; McDowell, R. S.; Goldblatt, M. *Inorg. Chem.* 1969, *11*, 2349.