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Resonance Raman Spectroscopy of Mass Selected Chromium Trimers in an Argon Matrix

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The resonance Raman spectra of mass-selected chromium trimers (Cr_3) in argon matrixes have been obtained. Five resonance Raman transitions were observed between 450 and 690 nm. Four of them are assigned to a totally symmetric (a_1') vibrational progression, from which we obtain a ground-state harmonic frequency of $\omega_e = 432.2$ cm^{-1} with $\omega_e x_e = 16.3$ cm^{-1}. The other Raman line, observed at 302.0 cm^{-1}, is assigned to the degenerate bending motion $\nu_2(e')$ of the triatomic metal cluster. The geometry of the ground state is that of an equilateral triangle (D_{3h}). These results provide a value of the stretching force constant of $k_e = 1.91$ mdyne/Å and a spectroscopic atomization energy of 0.36 eV.

Introduction

This work is an extension of our previous studies on transition metal trimers[1]. Cr is of special interest due to the great disparity between the relatively close d-orbitals and the diffuse nature of the s orbital. The ground-state configuration of Cr atom is $3d^5$-$4s^1$, which provides ample opportunity for multiple bonding, and increasing sophistication of our ability to carry out accurate calculations on these species encourages us to obtain accurate spectroscopic properties.

Transition metal clusters present particular experimental problems in that it is often difficult to obtain a sample of a particularly chosen cluster, free of contamination from other clusters of nearby nuclearity. Spectroscopic studies of such samples often lead to uncertainty in the exact nature of the observed species. We have solved this problem by construction of our mass-selection apparatus, which has provided unambiguous spectroscopic results.

In this work we obtain the absorption, and resonance Raman spectrum of mass-selected chromium trimers. The Raman spectrum consists of five lines, four of which form a progression that can be assigned to the symmetric stretch normal mode vibration. The remaining line can be assigned to the degenerate bend of an equilateral triangle (D_{3h}).

Experimental Section

Previous publications have described in great detail the instrumental setup of the CCNY metal cluster beam.[2,3] In this section we present a brief description of the experimental parameters employed by the apparatus for the formation, mass selection, deposition, and subsequent in situ resonance Raman spectroscopy of chromium trimers in an argon matrix. Chromium cluster cations are formed via argon ion plasma bombardment (at ~10 mA and accelerated at 25 keV) of a water-cooled chromium metal target (at 300 V) purchased from Goodfellow at 99.7% purity. A series of einzel lenses collect the chromium cluster ions from the sputtering region and focus the ions into the mass selection apparatus. Chromium trimers are then mass selected by a Wien filter. Most neutral chromium atoms produced during the sputtering process that traverse the Wien filter are lost to the system via a 10° bend of the path following mass selection.

Another set of einzel lenses focus the mass selected chromium trimer cations into the deposition region, where they are co-deposited with argon and electrons, for neutralization, onto a CaF_2 substrate. The Cr_3/Ar matrix is formed under cryogenic conditions (~16 K). Before actual deposition of Cr_3 onto the CaF_2 substrate, the trimers are slowed to ~10 eV, with respect to the potential across the metal target, by a Faraday cage encompassing the cooled CaF_2 substrate. This is done to ensure a soft landing of the mass selected sample onto the CaF_2 substrate. The current under hard landing conditions was measured to be 40 nA.

The chromium trimers were probed in situ via resonance Raman and absorption spectroscopy. The absorption spectrum for Cr_3 is obtained using scattering depletion spectrum (SDS). SDS is an absorption measuring technique in which a ratio between scattered light from the center of the CaF_2 substrate, where a majority of the sample is deposited, and scattered light from the edge of the substrate is obtained 90° from the incident radiation. The absorption spectrum (SDS) of chromium trimer in an argon matrix was acquired after a 5 h deposition of the molecule at an average current of 24 nA, giving a total concentration of ~120 nA h. As a check on our results, we separately deposited Cr_2 with a total concentration of 100 nA h. Although a distinct SDS spectrum of Cr_2 was obtained, no Raman intensity was observed. Consequently, we could not estimate the fragmentation ratio of Cr_3 to Cr_2 in the usual fashion. Crude estimates from the SDS spectra give a maximum fragmentation ratio of 10%.

Resonance Raman experiments were performed employing the visible lines of a Spectra Physics 2045 argon ion laser, as well as dye lasers utilizing R6G (spectral range ~ 575 to 622 nm), and DCM (spectral range ~ 630 to 685 nm) dyes. All Raman lines were detected with a Spex 1877E 0.6 m Triplemate Spectrometer coupled to a liquid nitrogen cooled CCD (Spectrum One and CCD30). All collected data was interpreted and displayed by DM3000R software interfaced with a computer.

Results

The resonance Raman spectrum of chromium trimer (Cr_3) isolated in an argon matrix at ~6 K is shown in Figure 1. All

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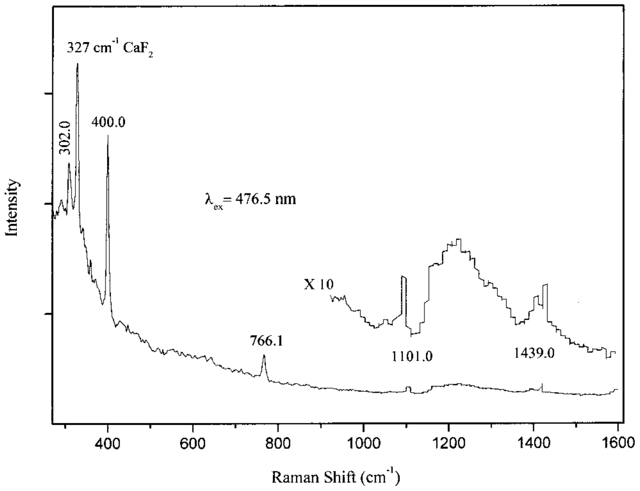

Figure 1. Resonance Raman spectrum of chromium trimer in an argon matrix at 16 K and excited at 476.5 nm. The line at 327 cm^{-1} is that of the CaF$_2$ substrate, and the band located at ~1225 cm^{-1} is attributed to fluorescence.

observed Raman frequencies are averaged over a maximum of 25 spectra in an exciting range of ~460 to 685 nm and are calibrated with respect to the 327 cm^{-1} Raman shift of the CaF$_2$ substrate. At an excitation wavelength of 476.5 nm, the isolated Cr$_3$ displays five distinct Raman lines. The observed frequencies of these lines are 302.0 (87), 400.0 (7), 766.1 (8), 1,100.8 (10), and 1,438.7 (16) cm^{-1}. No other lines were observed down to 100 cm^{-1}. The Raman line located at 400.0 cm^{-1} is the most intense of all the observable bands in our spectrum and we attribute the three Raman lines at higher frequencies, up to 1438.7 cm^{-1}, as a spectral progression in the 400.0 cm^{-1} frequency. Since this is the highest frequency fundamental, we assign the 400.0 cm^{-1} line to the totally symmetric stretch ν_1(a$'_1$) of chromium trimer.

Taking successive differences of Raman band centers and employing a least-squares fit (we have left out the line at 1438.7 cm^{-1} from this analysis, due to low signal-to-noise ratios), we obtain a ground-state harmonic frequency for this mode of ω_e = 432.2 (16) cm^{-1} with $\omega_e x_e$ = 16.3 (37) cm^{-1}. The other lower frequency Raman line, observed at 302.0 cm^{-1}, is assigned to the degenerate bending motion ν_2(e$'$) of the triatomic metal cluster. The frequency ratio of the two fundamentals 432/302 = 1.43 is sufficiently close to $\sqrt{2}$ to indicate that the symmetry of chromium trimer is D_{3h}, confirming the assignment to the degenerate bend. A summary of our assignment for this spectrum is given in Table 1, and values for all spectroscopic constants for this system, namely the ground-state vibration for Cr$_3$ (ω_e), the anharmonicity ($\omega_e x_e$), the force constant (k_e), and the atomization energy ($\boldsymbol{D}_e{}^a$) are given in Table 2. Note that, as in the dimer, the force constant for the trimer (1.91 mdyne/A) is rather large, suggesting considerable involvement of d electrons in bonding. However, the energy of atomization (0.36 eV) is quite low. Such considerations led Casey and Leopold[4] to suggest that the potential governing nuclear motions in the dimer deviates considerably from that of a Morse curve. It is likely that the trimer potential energy surface is similarly distorted.

We also observe an absorption spectrum for Cr$_3$ in the form of a scattering depletion spectrum, as shown in Figure 2. The absorption of Cr$_3$ displays noticeable absorption bands in an exciting region of ~400 to 685 nm. The positions of these absorption bands are given in the figure. Plotted parallel with the SDS spectrum for chromium trimer are the resonance Raman excitation profiles of the 400.0 and 302.0 cm^{-1} lines. The excitation profiles show significant resonance Raman enhancement of the 400.0 cm^{-1} line in the absorption region of ~461 and 477 nm. We were unable to probe the absorption region between ~525 to 575 nm due to the unavailability of dyes in this region. The 302.0 cm^{-1} line, ν_2(e$'$) vibration, shows relatively strong resonant enhancement at ~604 and 647 nm. This indicates the existence of strong vibronic coupling in the excited state of these two optical transitions.[5] This conclusion is also likely for the 477 nm transition.

TABLE 1: Summary of Observed Resonance Raman Frequencies for Cr Clusters from Various Laboratories

frequencies (cm^{-1}) and assignments for mass selected Cr$_3$ (this work)		frequencies (cm^{-1}) and assignments for non mass-selected Cr clusters[a]		
frequencies	Cr$_3$	frequencies	Cr$_2$	Cr$_3$
		123		ν_3
		145		
		155	A(0−0)	
		226		ν_2
302.0	ν_2(e$'$)			
		308		ν_1
400.0	ν_1(a$_1$)	396	ν_1	
		439		
		548	A(0−1)	
		620[b]		
766.1	2ν_1	770[b]	2ν_1	
		919	A(0−2)	
1101.0	3ν_1	1100[b]	3ν_1	
1439.0	4ν_1	1410[b]	4ν_1	

[a] See refs 6 and 9. [b] Estimated from published spectrum in ref 6.

TABLE 2: Spectroscopic Constants Obtained from Cr$_3$ Resonance Raman Spectra

ω_e (cm^{-1})	$\omega_e x_e$ (cm^{-1})	$\boldsymbol{D}_e{}^a$ (eV)	k_e (mdyne/Å)
432.2 (16)	16.3 (4)	0.36	1.90

Upon deposition of Cr$_2$ we found no Raman transitions despite an intensive search across the excitation region. We take this to mean that there is little or no resonance enhancement of the dimer lines. A portion of the absorption (SDS) spectrum is shown for Cr$_2$ in Figure 2. Note there is overlap of dimer and trimer absorption in the region of 450 to 500 nm, but that the

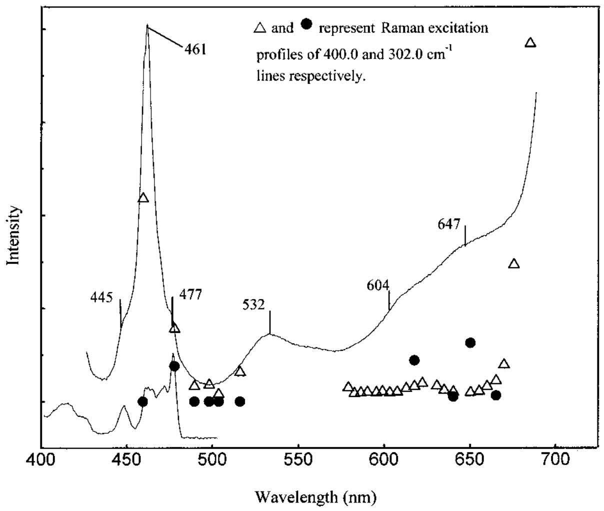

Figure 2. The absorption (SDS) spectrum of Cr$_3$ in an argon matrix. Plotted parallel with the trimer absorption spectrum is the resonance Raman excitation profile of the 400.0 (△) and 302.0 (●) cm^{-1} lines. In the lower left corner, from 400 to 500 nm is a truncated absorption (SDS) spectrum of Cr$_2$ in an argon matrix at 16 K. The vertical lines refer to relative absorption maxima.

spectra are clearly distinct. There is no measurable intensity for Cr_2 at longer wavelengths.

Discussion

Using resonance Raman spectroscopy, DiLella et al.[6] examined a mixture of chromium metal clusters. These molecules were formed by sublimation and subsequent condensation with Ar, Kr, and Xe onto a polished aluminum surface (~12 K). Upon excitation at 514.5 nm, they observed 13 spectral lines that we have listed in Table 1 along with our results. They found two major progressions that began with fundamentals located in their spectrum at 308 and 396 cm^{-1}.[6] One progression (396 cm^{-1}) may be characterized by vibrational constants $\omega_e = 427.5$ cm^{-1} and $\omega_e x_e = 15.75$ cm^{-1} and was assigned to the dimer, and the other, based on a line at 308 cm^{-1}, gave vibrational constants $\omega_e = 313$ cm^{-1} and $\omega_e x_e = 2$ cm^{-1}.[6] Since this latter progression (along with lines at 226 and 123 cm^{-1}) increased in intensity simultaneously upon illuminating a more metal-rich portion of the sample, they assigned these lines to the trimer. In addition, a progression with an origin at 155 cm^{-1} was assigned (in a later work) to an excited state (A) of the dimer.[6]

Through pulsed YAG laser vaporization of chromium metal, Bondybey and English[7]observed a fluorescence excitation spectrum for Cr_2. On the basis of their interpretation of the high resolution spectrum, they were certainly viewing emission due to Cr_2, i.e., alternate rotational lines were missing from the spectrum, and only the P and R branches were present. From their observed gas-phase emission spectrum, Bondybey and English derived $\Delta G_{1/2} = 452.34$ cm^{-1} and a ground-state vibrational frequency for the dimer to be $\omega_e \sim 470$ cm^{-1}. Our inability to observe resonance Raman intensity in Cr_2 is also consistent with their observation that there is practically no change in bond length (0.004 Å) in the X to A transition. This would imply extremely small Franck−Condon factors in the resonance Raman spectrum.

The above value for ω_e (470 cm^{-1}) was confirmed in the negative ion photoelectron spectroscopy of Casey and Leopold.[8] Their extensive study resulted in the conclusion that the ground state of Cr_2 has a potential curve that deviates strongly from a Morse potential. To explain the observed vibrational spectrum, they had to assume a "shelf" like addition to the curve and required terms up to order $(v + 1/2)^6$ to obtain an adequate fit. Their value of $\omega_e = 474.3$ cm^{-1} is in excellent agreement with that of Bondybey and English and in marked contrast with that of DiLella et al.[6] In a subsequent paper, Moskovits, Limm, and Mejean[9] revisited the spectrum of Cr_2 and concluded that the discrepancy between the gas-phase results and their matrix isolation results ($\omega_e = 425$ cm^{-1}) are due to an unusually large matrix shift. Usually matrix effects shift observed vibrational frequencies by 1−2%, so that a shift of almost 10% must be considered quite large.

Our results presented here clear up this discrepancy. With the advantages provided by mass selection we have shown that, in an argon matrix, Cr_2 has no resonance enhancement. The observation by DiLella et al.[6] of a progression based on 396 cm^{-1} and attributed to the dimer is nearly identical to the lines observed in our trimer spectrum (see Table 1). We recommend that our assignment of the 400.0 cm^{-1} progression as the totally symmetric stretch of chromium trimer is indeed the correct assignment for this progression. It is likely that the dimer was not observed by DiLella et al.,[6] since we see no resonance enhancement in our mass-selected dimer deposit. Despite this conclusion, we should note that the analysis of DiLella et al. was strengthened by a careful isotope effect calculation (including the effects of mass on $\omega_e x_e$) of the high-resolution spectrum they attributed to the dimer.[6] A similar analysis for the (D_{3h}) trimer failed to fit their observed spectrum. We have been unable to confirm their results since we do not observe these isotopic lines in our spectrum. It is possible that their isotopic lines were complicated by matrix site effects which were persistent despite their attempts to anneal the sample, although this explanation requires a rather remarkable coincidence. Despite this discrepancy, we feel that the mass-selection afforded in our experiments remains strong evidence that we are in fact observing the trimer spectrum, and that DiLella et al. misassigned this as the dimer.[6]

TABLE 3: Summary of Observed and Predicted Force Constants, k_e, for Various Clusters of Cr (Note that predicted k_e values are based upon rules of Ozin and MacIntosh.[14])

cluster	observed k_e (mdyne/Å)	predicted k_e
Cr_2	3.45	(3.45)
Cr_3 (D_{3h})	1.91	1.73
Cr_4 ($\boldsymbol{T_d}$)	1.29[a]	1.15
Cr_4 (D_{2d})	0.97[a]	1.15/1.38[b]

[a] We are assuming the 308 cm^{-1} band represents the totally symmetric stretch of each symmetry and that all stretching constants are equal. [b] The predicted force constant values for diagonal/edge bonds of planar rhombus.

It should be noted that the line we observe at 302.0 cm^{-1}, assigned to the e′ vibration, is not the same as that observed by DiLella et al.[6] at 308 cm^{-1}. The latter is considerably more intense relative to the 396 cm^{-1} in their spectrum. Our observed Raman line at 302.0 cm^{-1} is quite weak, with respect to the 400.0 cm^{-1} line, and has a very different excitation profile (see Figure 2).

In a far IR study of matrix isolated Cr_3, Ozin and Mitchell[10] observed over fifteen distinct lines in the range 95 to 325 cm^{-1}. They attributed these lines to numerous sites with distinct angular geometries. Since the totally symmetric vibration was not observed in their experiments, they had no independent measure of the stretching force constant, and assumed $f_r = 1.00$ mdyne/Å, far lower than we observe here (Table 3). However, our degenerate bending vibration falls within their range of observation. We only see evidence for one site. Because our Cr_3/Ar matrix is grown at a much slower rate than that of Ozin and Mitchell,[10] most likely our samples had sufficient time to attain the most stable configuration.

In a recent work, Alex, Green, Millam, Villalta, and Leopold[11] examined the negative ion photoelectron spectroscopy of mass-selected Cr_3. They observed vibrational spacings in the lowest transition of 480(15) cm^{-1} and 130(15) cm^{-1}, which differ considerably from the results observed here. Most likely they are observing transitions to a different state than we are, since the geometry derived from these frequencies cannot be D_{3h} and the force constants should also be quite different.

Derouault and Dalibart[12] carried out experiments involving acquisition of UV−visible absorption spectra, Raman scattering spectra, and luminescence spectra of highly concentrated chromium fragments vaporized from a tungsten basket and cooled to 12 K in an argon matrix. Using factor analysis methods on the acquired data they resolved the spectra into seven absorption profiles labeled N1 to N7. Derouault and Dalibart assigned absorption spectra N2, N3, and N4, which gave absorption bands in the 330 nm range, to Cr atoms in different argon sites.[12] Absorption profile N1 was assigned to an excited state of Cr, and absorption spectrum N7 was attributed to Cr_2. They made this assignment based on previous absorption profiles obtained by Klotzbucher and Ozin[13] on chromium dimers and trimers in argon matrixes. Klotzbucher and Ozin observed low energy optical absorptions for Cr_2 at 460/469 nm and for Cr_3 at 477 nm.

Comparing our absorption (SDS) profiles for both chromium dimer and trimer to Derouault and Dalibart's absorption spectra N5 (assigned Cr_3), N6 (assigned Cr_2-Cr), and N7 (assigned Cr_2), there are clear similarities. We observe the 469 nm absorption band for Cr_2 in our absorption (SDS) spectrum, which they observe in their N6 (assigned Cr_2-Cr) absorption spectrum. The 477 nm absorption band that is observed for both chromium dimer and trimer in our absorption (SDS) spectrum is similar to Derouault and Dalibart's N7 (assigned Cr_2) absorption spectrum. It is therefore likely that the 477 nm absorption as initially observed and attributed to Cr_3 by Klotzbucher and Ozin is correct.[13] This would imply the assignment of spectrum N7 to chromium trimer instead of chromium dimer. This is also consistent with our reassignment of the Raman spectrum of DiLella et al.[6] This line of reasoning would also imply assignment of spectra N5 and N6 to a chromium molecule of higher nuclearity, possibly Cr_4, and chromium dimer with a small mixture of the atom, respectively.

Clearly, if the above analysis is correct, the lines at 123, 226, and 308 cm^{-1} assigned by DiLella et al.[6] to the trimer of chromium, must be some other species. Since these Raman lines appear in regions of their chromium sample more rich in metal, it is likely that these lines are due to chromium clusters of higher nuclearity. The most likely candidate is the tetramer, Cr_4. If the tetramer is a tetrahedron we expect three distinct fundamentals $\nu_1(a_1)$, $\nu_2(t)$, and $\nu_3(e)$, which should have the frequency ratios of $2:\sqrt{2}:1$, respectively; however, $\nu_1/\nu_2 = 308/226 = 1.38$ and $\nu_1/\nu_3 = 308/126 = 2.46$, and thus the tetramer must deviate significantly from a tetrahedral structure. A square planar structure can also be eliminated since all the frequencies should be nearly equal. Another symmetric possibility is a planar rhombus (D_{2h}). For such a structure, there should be six distinct fundamentals. Two are of $\boldsymbol{A_g}$ symmetry and should be observed in resonance Raman spectroscopy, while those of $\boldsymbol{B_{1g}}$, $\boldsymbol{B_{2g}}$, and $\boldsymbol{B_{3g}}$ symmetry should be Raman active. Assuming all bonds have an equal force constant, the frequency ratios for $\nu_1(\boldsymbol{A_g})$: $\nu_2(\boldsymbol{A_g})$: $\nu_3(\boldsymbol{B_{1g}})$ should be $3^{1/2}/\sqrt{2}/1$, (i.e., 1.73/1.41/1), still considerably different from the observed ratios. Either there is a considerable difference between the rhomboidal diagonal bond force constant and the edge bond force constant, or other possible geometries must be considered.

Examining the ratios observed, we might guess that the correct geometry lies somewhere between a rhombus and tetrahedron. We can envision, for example, a planar rhombus in which one atom bends out of plane dihedrally in C_{2v} symmetry until it reaches an apex on top of the remaining three atoms forming a tetrahedron. Normal mode calculations indicate that the vibrational frequencies should vary monotonically between these two limits, but, as of now, there is insufficient data observed to obtain a complete analysis.

In the two limits, however, it is possible to calculate bond stretching force constants assuming the totally symmetric stretch is at 308 cm^{-1}. For a tetrahedron we obtain $k_e(4) = 1.29$ mdyne/Å. For a rhombus (assuming all bonds with equal force constant) $k_e(4) = 0.97$ mdyne/Å. Using the rules of Ozin and McIntossh,[14] as mentioned above, we can predict the expected force constants. For a tetrahedral cluster, Cr_4 (T_d), we expect $k_e(4) = 1/3\ k_e(2) = 1.15$ mdyne/Å For a planar rhombus, Cr_4 (D_{2h}), we expect $k_e(4) = 1/3\ k_e(2) = 1.15$ mdyne/Å for the diagonal bond and $k_e(4) = 2/5\ k_e(2) = 1.38$ mdyne/Å for the edge bonds. These results are summarized in Table 3. We see once again that neither the rhomboidal nor the tetrahedral geometry is likely, but that some intermediate (C_{2v}) geometry may be correct. Note, however, that the predicted force constants and the observed force constants are sufficiently close in magnitude to lend support for the assignment of these lines to the tetramer. The only other set of metal clusters for which so much information is known about the small cluster force constants is tantalum.[5]

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