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Raman Spectrum of Mass-Selected Terbium Dimers in Argon Matrixes

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We report on the absorption, resonance Raman, and Raman excitation profile spectra of mass-selected terbium dimers in argon matrixes. An absorption band found between 620 and 680 nm was assigned to terbium dimers. The Raman excitation profile of dimer frequencies resembles closely this absorption spectrum. Unlike other lanthanide dimers, resonance Raman spectra of terbium dimer, obtained by excitation into this region with tunable dye laser radiation, gives two progressions with one up to 7 Stokes transitions, and the other up to 4 transitions. We interpret these to represent two distinct electronic states X and A. For the ground (X) state, we obtain $\omega_e = 137.6 \pm 0.4$ cm^{-1} with $\omega_e x_e = 0.31 \pm 0.05$ cm^{-1}, leading to a spectroscopic dissociation energy of 1.9 ± 0.3 eV, force constant $k_e = 0.88 \pm 0.01$ mdyn/Å. The first electronic (A) state has an origin at 313.9 cm^{-1} with a progression in $\omega_e = 136.3 \pm 0.2$ cm^{-1} and $\omega_e x_e = 0.14 \pm 0.05$ cm^{-1}, leading to an excited-state spectroscopic dissociation energy of 4.1 ± 1.2 eV.

Introduction

In this article we extend our recent investigations of the Raman spectroscopy of lanthanide dimers[1−3] to Tb_2. Relatively little previous work has been carried out on this molecule. In 1972, J. Kordis[4] et. al measured the dissociation energy by means of a Knudsen effusion mass spectrometric study. This work was confirmed by Kant and Lin[5] at around the same time.

We report the observation of resonance Raman spectra, the absorption ("scattering depletion") spectrum, and the Raman excitation profile of mass-selected Tb_2 in argon matrixes. From the absorption (scattering depletion) spectrum, one optical transition in the region 623−673 nm was observed. By excitation into this region with dye laser radiation, two Raman series were observed, with one up to 7 Stokes transitions, and the other up to 4 transitions. These data give for the ground (X) state $\omega_e = 137.6 \pm 0.4$ cm^{-1} with $\omega_e x_e = 0.31 \pm 0.05$ cm^{-1}, leading to a spectroscopic dissociation energy of 1.9 ± 0.3 eV, force constant $k_e = 0.88 \pm 0.1$ mdyn/Å, and the other progression has an origin at 313.9 cm^{-1}, the progression 450.0, 585.9, 721.4 cm^{-1}, which gives $\omega_e = 136.3 \pm 0.2$ cm^{-1} with $\omega_e x_e = 0.14 \pm 0.05$ cm^{-1}, leading to a spectroscopic dissociation energy of 4.1 ± 1.2 eV, which we assigned to an excited (A) state.

Experiment

The CCNY cluster deposition source has been described in detail elsewhere.[7,8] Briefly, an argon ion beam (typically 10 mA at 25 keV) sputters a cooled, terbium target (Alfa Aesar, 99.9% (REO)). The sputtered products are extracted by electrostatic lenses, mass-selected using a Wien filter, bent by 10° to eliminate neutrals (produced during sputtering), and then guided and focused by an einzel lens into the deposition region. Terbium dimer (or atomic) ions were then co-deposited with argon gas and electrons onto a ∼16 K CaF_2 plate substrate. Prior to deposition, the selected ions were simultaneously slowed to 15 eV by a surrounding "Faraday cage " to ensure a soft landing. Ion currents under hard landing conditions ($V_{dep} = 300$ V) could be measured on the Faraday plate in the deposition region and were Tb^+ (110 nA), Tb_2^+ (25 nA). Matrixes were grown at about 6 μm/h with an Ar:metal ratio of approximately 10^4:1. By comparing the intensities of known atomic excitation features in a dimer deposition with those obtained from deposition of atom under similar conditions, the dimer fragmentation is estimated to be less than 10%.

Matrix samples were interrogated in situ using both absorption and Raman spectroscopy. As previously described,[7,8] the absorption measurements were made by collecting the light at 90° to that incident, a technique we term "scattering depletion spectroscopy" (SDS). Raman spectra were recorded using a dye laser (Coherent, model CR599) with DCM, pumped by the "green-blue" lines of an argon ion laser (Spectra Physics 2045) for excitation. Raman excitation profiles were obtained by observing the Raman spectra while tuning the dye laser in small steps through the absorption region 620−680 nm. Scattered light was collected at 90° into a Spex 1877E 0.6 m Triplemate Spectrometer and detected by a liquid nitrogen cooled CCD detector (Spex model "Spectrum One", and CCD30) with DM3000R software connected to a computer. All Raman results were calibrated using the CaF_2 (substrate) line at 327 cm^{-1}. The absorption (SDS) spectrum was recorded following a 5 h deposition of 18 nA of Tb_2.

Spectra and Analysis

A portion of the absorption spectrum, shown as Figure 1 contains the only absorption features that we could definitely assign to the dimer. This assignment is verified by the observation of resonance Raman spectra for excitation into these bands. The Raman excitation profiles, obtained by dividing the Raman intensity (of the first Stokes line) by the intensity of the CaF_2 Raman line, are superimposed in this figure.

Raman spectra were observed throughout the region 623−673 nm, Figure 2 shows a typical Raman spectrum (excited at 652.7 nm) for a 90 nA-h sample of diterbium in argon matrixes.

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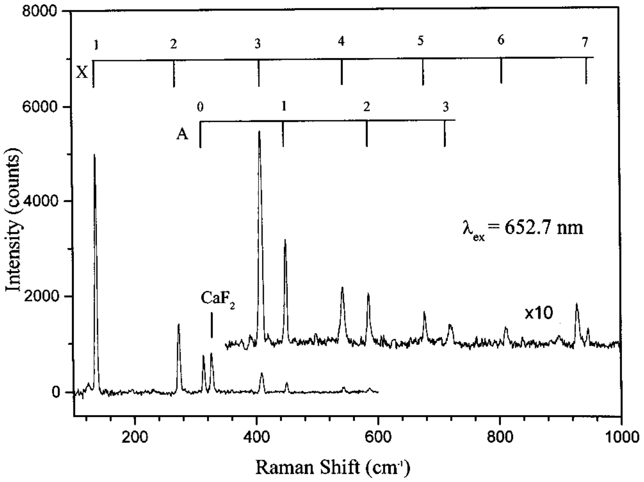

Figure 1. Resonance Raman spectrum (λ_{ex} = 652.6 nm) of terbium dimer in argon matrixes.

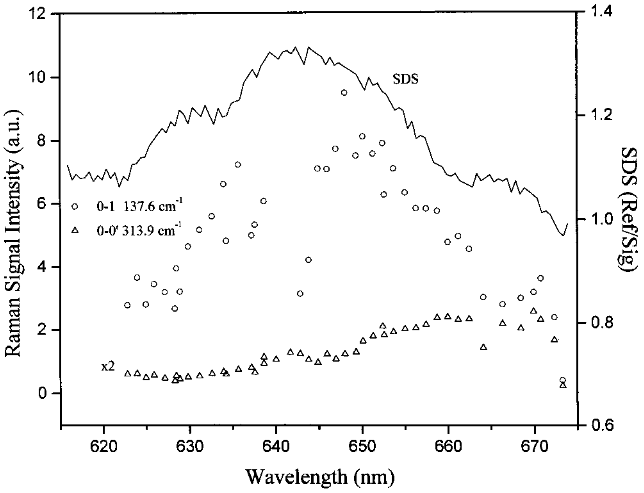

Figure 2. Absorption (scattering depletion) spectrum (right-hand scale) and Raman excitation profile for ground-state (X) and excited-state (A) transition of terbium dimers in argon matrixes.

A nonresonant Raman line at 327 cm^{-1} due to the CaF$_2$ substrate is also in evidence and is used as a wavelength calibration. The Raman spectrum consists of two distinct progressions, the average Raman shift over 47 spectra at different wavelengths (between 623 and 673 nm) is listed in Table 1 and Table 2.

These data give for the ground (X) state $\omega_e = 137.6 \pm 0.4$ cm^{-1} with $\omega_e x_e = 0.31 \pm 0.05$ cm^{-1}, leading to a force constant $k_e = 0.88 \pm 0.01$ mdyn/Å, and spectroscopic dissociation energy of 1.9 ± 0.3 eV. Our value for the dissociation energy is only slightly higher than that obtained by the third law techniques by Kant and Lin[5] which is 1.4 ± 0.3 eV or that obtained by Kordis and Gingerich,[4] which is 1.33 ± 0.26 eV. The latter also use the Guggenheimer[8] method to predict an $\omega_e = 135$ cm^{-1} in good agreement with our experimental results.

The lines in Table 2 are assigned to a low lying electronic (A) state at $T_0 = 313.9$ cm^{-1}, with $\omega_e = 136.3 \pm 0.2$ cm^{-1}, and $\omega_e x_e = 0.14 \pm 0.05$ cm^{-1}, leading to a spectroscopic dissociation energy of 4.1 ± 1.2 eV.

As can be seen from Figure 1, the Raman excitation profile of the ground X state is almost identical to the absorption spectrum (SDS), and in fact appears more sensitive. The bands are centered at approximately 633 and 645 nm. The excitation profile of the origin band of the A transition, though much less sensitive, appears to have a somewhat different profile, peaking at longer wavelength. Due to the low signal/noise ratio of this spectrum it is not possible to draw any reliable conclusions from this.

TABLE 1: Vibrational Progression for the Ground (X) State of Tb$_2$

v''	1	2	3	4	5	6	7
Raman shift (cm^{-1})	137.6	273.6	409.3	544.5	679.2	813.5	946.3

TABLE 2: Vibrational Progression for the First Excited (A) State of Tb$_2$

v'	0	1	2	3
Raman shift (cm^{-1})	313.9	450.0	585.9	721.4

Discussion

Terbium lies next to gadolinium in the periodic table. The ground-state configuration of Tb atom is [Xe] 4f^{9}6s^2 while that for Gd is [Xe] 4f^{7}5d^{1}6s^2.The promotion energy for 4f^{9}6s^2 → 4f^{8}5d^{1}6s^2 in Tb (utilizing only the lowest spin−orbit levels) is only 0.035 eV. Thus it is not surprising that the dimer force constants are almost identical: k_e = 0.88mdyn/Å for Tb$_2$ while k_e = 0.89mdyn/Å for Gd$_2$.[3] Both force constants are comparable to that for Y$_2$ (0.90mdyn/Å)[9] and therefore most likely correspond to a bond order of 1. The lack of ability to form stronger bonds, as for example in La$_2$[1] (k_e = 2.28mdyn/Å) can at least partly be attributed to the rather high 6s → 5d promotion energies, 1.87 eV and 0.79 eV for Tb and Gd, respectively. The 6s → 5d promotion energy is likely to be important since a 6s^1 configuration is thought to promote stronger chemical bonding. La, for example, has a promotion energy of only 0.33 eV, leading to a likely bond order of more than two.

Note that although the observed first excited (A) state lies only at T_0 = 313.8 cm^{-1}(0.039 eV) above the ground state, its dissociation energy (4.1 eV) is considerably higher. It is thus likely that the excited state dissociates to atomic states separated by 2.2 eV (4.1−1.9 eV) from those of the ground state. It is possible that the s → d promotion energy for one atom 1.9 eV accounts for this difference. It is consistent then to postulate that the ground state arises from two ground-state 4f^{9}6s^2 (or 4f^{8}5d^{1}6s^2) atoms while the first excited state from one 4f ^{9}6s^2 (or 4f^{8}5d^{1}6s^2) and one 4f^{9}5d^{1}6s^1 (or 4f^{8}5d^{2}6s^1) atom.

Dolg, Stoll, and Preuss[10] have carried out density functional calculations employing psuedopotentials with configuration−interaction on homonuclear diatomic lanthanides. For all the dimers, they predict several low lying states. Most important among these are a $^5\Sigma_u^-$ state from a $4f^n 4f^n \sigma_g^2 \sigma_u^1 \sigma_g^1 \pi_u^2$ state configuration, as well as a $^1\Sigma_g^+$ from a $4f^n 4f^n \sigma_g^2 \sigma_u^2 \sigma_g^2$ configuration. Their results indicate the $^5\Sigma_u^-$ to be the ground state in Tb$_2$. Our results would tend to confirm this prediction in that the $^5\Sigma_u^-$ has a lower formal bond order (and vibrational frequency) than the $^1\Sigma_g^+$ state. This raises the question as whether the A state may be the $^1\Sigma_g^+$. This assignment is somewhat less likely, since the vibrational frequency observed is not much different than that of the ground state, although the dissociation energy is much larger. Clearly a more detailed theory is in order to establish firmly the nature of these states.

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